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ERRATA:

Vol. 63, 1938:

p. 869. Line 8 from bottom. *For* "Present-day fertilisers contain very little chloride" *read* "Present-day fertilisers containing nitrate contain very little chloride."

Vol. 64, 1939:

p. 22. Line 14. *For* M ± 6 *read* M ±.
Line 24. *For* 2 × P.E. *read* 3 × P.E.
Line 25. *For* 2·576 *read* 3·864.

p. 66. Line 23. The figures should read: 0, 0·5, 0·001; 0, 0·34, 0·005; 0·95, 0·69, 0·91; 1·89, 1·90, 0·03; 1·92, 3·14, 0·05.

p. 133. Line 6 from bottom. *For* "2 litres of water are added" *read* "made up to 2 litres."

p. 134. Line 1. *For* "in strong daylight" *read* "strong daylight being avoided."

p. 134. Line 18. The prescription of 50 ml. is unnecessary.

p. 135. *For* "0·2G^2" *read* "0·02G^2."

p. 182. Line 1. *For* "0·1622 molar" *read* "0·01622 molar."

p. 675. Line 13. *For* "0·02" *read* "0·25 ml."

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, December 7th, 1938, the President, Professor W. H. Roberts, in the chair.

Certificates were read in favour of G. Carter, B.Sc., A.I.C.; O. B. Darbishire, B.Sc., A.R.C.S., D.I.C., A.I.C.; F. M. Dyke, B.Sc., F.I.C.; A. A. Eldridge, B.Sc., F.I.C.; Prof. F. Feigl, Dr. Ing.; G. H. Fraser; M. B. Ichaporia, M.Sc., Ph.D., A.I.C.; R. Porter; A. C. Ratcliff, B.Sc.; W. H. Templeton, B.Sc., F.I.C.

The following were elected members of the Society:—W. A. Alexander, B.Sc., A.I.C.; D. R. A. Davies, B.Sc.; E. R. Jones, B.Sc., Ph.D., F.I.C., M.D., Ch.B., D.P.H.; H. A. Jones, A.I.C.; Dr. B. A. Macola; J. M. Malcolm, A.I.C.; Mrs. S. M. L. Tritton, M.P.S., F.I.C.; S. A. Ullah, B.Sc., Ph.D., A.I.C.

The following papers were presented and discussed:—"The Selective Oxidation of Animal and Vegetable Fats: A New Constant," by W. A. Alexander, B.Sc., A.I.C.; "The Determination of the Essential Oils of White and Brown Mustards," by R. C. Terry, M.Sc., A.I.C., and J. W. Corran, Ph.D., F.I.C.; "The Electrolytic Determination of Bismuth," by F. G. Kny-Jones, M.Sc.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on October 22nd, 1938. The Chairman (Prof. T. P. Hilditch) presided over an attendance of thirty-seven, which included the President (Professor W. H. Roberts), who introduced a discussion on the Food and Drugs Act, 1938, in which many members took part.

The following communications were made and discussed:—"A Note on Nigerian Ginger," by P. H. Jones, F.I.C., and a paper on the "Quantitative Determination of Mercury in its Compounds with Special Reference to the Assay of Solution of Mercuric and Arsenious Iodide," by H. Brindle, B.Sc., F.I.C., Ph.D., and C. E. Waterhouse, A.I.C., Ph.D.

A Meeting of the Section was held in Manchester on December 10th, 1938. The Chairman (Prof. T. P. Hilditch) presided over an attendance of thirty-nine.

The following papers were read and discussed:—"The Estimation of Vitamins and Hormones," by R. A. Morton, Ph.D., D.Sc., F.I.C.; "A Note on the Behaviour of Rice Bran," by C. Louden, B.Sc., F.I.C., and F. L. Kinsella; "A Convenient Method of Estimating the Hydrocyanic Acid generated by Linseed Cake," by C. Louden, B.Sc., F.I.C., and H. Antrobus.

Resolutions were passed congratulating Mr. U. A. Coates on the occasion of the diamond jubilee of his wedding day, and Mr. H. Humphreys Jones on his appointment as a Justice of the Peace.

SCOTTISH SECTION

An Ordinary Meeting of the Section was held in the Central Station Hotel, Glasgow, on November 18th, 1938. The meeting was of an informal nature and the following subjects were discussed:—"American Food and Drugs Act," introduced by R. G. Thin; "Copper Content of Tomato Purée," introduced by A. Dargie; "Memorandum on the Food and Drugs Act, 1938," introduced by M. J. Robb; "Determination of Alumina in Water," introduced by R. T. Thomson; "Determination of Lactose and Sucrose in Milk Chocolate," introduced by H. C. Moir; "Air Raid Precautions," introduced by J. W. Hawley.

A new Colour Reagent for Lead and its Use as an Indicator in the Titration of various Cations and Anions*

(Pb, Zn, WO_3, MoO_3, V_2O_5, P_2O_5, As_2O_5)

By B. S. EVANS, M.C., M.B.E., D.Sc., F.I.C.

(*Read at the Meeting, October* 5, 1938)

Colour reactions for lead, due to the formation of soluble compounds with the range of stability necessary for indicator purposes, are rare.[11] The well-known colour formed with diphenyl thiocarbazone[1,9] is intense and easily produced, but it is so stable as to preclude its use as an indicator. Carbazones give relatively intense colours with many metals, including lead, copper,[9] iron, nickel, cobalt, zinc, mercury,[10,2,3] thallium[4] and others, but here again the lead colour is so stable that it is not readily destroyed by most precipitants. It was observed that if an acetone solution of diphenyl carbazide is added to a solution of lead nitrate containing pyridine nitrate a very pale pink colour is produced; if the solution is allowed to stand the colour slowly deepens, becoming eventually (after about 20 hours) a dark red, proportional in depth to the amount of lead present. After a considerable amount of work a reagent was evolved which immediately developed the full colour.

Reagent.—The reagent used in the work done for this paper was prepared as follows:

Solutions required.—(*a*) A 1·5 per cent. solution of diphenylcarbazide in alcohol (this solution seems to keep its properties indefinitely, although it darkens and the carbazide is probably converted into carbazone); (*b*) purified pyridine (*vide infra*); (*c*) dilute nitric acid (sp.gr. 1·2).

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* Communication from the Research Department, Woolwich.

A mixture of 10 ml. of (*a*) with 30 ml. of (*b*) was diluted with 120 ml. of cold water, 2 ml. (carefully measured) of (*c*) were added, and the liquid was heated to boiling and allowed to stand on the bench overnight, after which it was ready for use. It has subsequently been found that the heating is entirely unnecessary, and it has consequently been discontinued; the reagent is now prepared as follows:

Preparation.—A mixture of (*b*), (*c*) and water in the correct proportions is made up in bulk, and to the required volume of this mixture an amount of (*a*) is added to produce the strength indicated above. The liquid is allowed to stand overnight and is then ready for use. With a fairly new (*a*) solution the colour directly after mixing will probably be very pale; if a test is made with it on a lead nitrate solution the colour produced is almost imperceptible at first, but gradually deepens to the full shade if allowed to stand for some hours. After the reagent has stood for its appointed time its colour is a fairly deep orange-brown, and on being mixed with lead nitrate solution it should develop its full colour (a cherry-red with 1·0 mg. of lead nitrate in 100 ml. of water) immediately. The reagent keeps fairly well for several days, but it slowly deteriorates and eventually ceases to give any red colour whatever with lead. Since the completion of the work for this paper, however, I have found that an alcoholic solution of diphenyl carbazide which has been made up for several weeks (in one instance five) produces a reagent which can be used without any standing (presumably because the carbazide has been oxidised to carbazone). If only fresh carbazide solution is available the lead and zinc colours can be developed by the cautious addition, drop by drop, of bromine water to the liquid after the addition of the reagent (for lead, until the full colour is produced ; for zinc, 5 drops). A satisfactory reagent seems also to be produced by warming 2 ml. of the carbazide solution with 1 drop of hydrogen peroxide (20 vols; stabilised with sulphuric, *not* with phosphoric acid) until the brown colour ceases to deepen, and then mixing with 30 ml. of the pyridine-nitric acid-water mixture. These oxidising agents, however, are very liable to destroy the properties of the reagent altogether if used in slight excess, and on the whole it is better to prepare the reagent by the method given above.

THE TEST.—If a small amount of lead nitrate solution is neutralised and diluted to about 100 ml., and 10 ml. of the reagent are added, the red colour developed is proportional to the amount of lead present; with 0·002 g. of lead nitrate the colour should be a fairly dark cherry-red; a blank test done in the same way, but without lead, gives a pale orange-brown due to the colour of the reagent. The colour difference is made more apparent by adding acetone, which seems to eliminate the reddish factor from the reagent colour without disturbing that due to the lead; the colours are now a permanganate tint and a very pale yellow, respectively. If, to the solution containing the developed lead colour, successive additions of very dilute nitric acid are made, it first turns paler and then at a certain point is entirely bleached; if, instead of nitric acid, dilute ammonia is added, the colour first darkens and then at a certain point is replaced by the orange-brown shade characteristic of alkaline solutions of diphenylcarbazide. There is thus a *p*H range over which the colour is effective and a fairly limited one at which it is at an optimum; this is the reason why the 2 ml. of nitric acid added to the reagent must be carefully measured and why the lead solution has to be neutralised before making the test. The colour seems to be destroyed by anything liable to precipitate lead under the *p*H conditions prevailing; thus phosphates, arsenates, tungstates, vanadates, molybdates and citrates destroy it promptly, and sulphate in any appreciable amount weakens it. It is this fact that makes the colour reaction interesting, because so many other metals give a similar colour (*vide infra*) that it is not of much use as a test for lead; but if the colour can be progressively removed by addition of small amounts of any of the reagents mentioned above (*i.e.* by titration), it can obviously be made the basis of a volumetric process for minute amounts of lead; on the other hand, it should equally be possible to use it as an indicator in the titration of these reagents with lead nitrate solution. The following method has been worked out for the volumetric determination of lead:

VOLUMETRIC PROCESS FOR LEAD.—The solution of lead as nitrate, neutralised (to litmus paper) with ammonia, is placed in a flask and diluted to 100 ml.; 100 ml. of distilled water are placed in a similar flask; 10 ml. of reagent are added to each, followed by 30 ml. of acetone. The titrating liquid is prepared in the following manner:—Ten ml. of syrupy phosphoric acid are made up to 100 ml. (A); 20 ml. of (A) are made up to 250 ml. (B); 10 ml. of (B) are diluted, boiled, cooled and made up to 1000 ml. (C).

The lead colour is titrated away with solution (C) until the colours of the supernatant liquids in the two flasks match. The colour at first diminishes rapidly, but towards the end-point the change becomes slower; there is no difficulty with the titration up to within about 0·4 ml. of the end-point; from then onwards the colour change is very slight and gradual; the presence of the slightly brownish precipitate of lead phosphate somewhat complicates the matching, and when matching becomes difficult it is desirable to allow the liquid to stand for a minute or two after each addition. The end-point, however, can be determined with reasonable speed and certainty. The titration can be performed as accurately in the absence of acetone, but it then becomes much slower as, towards the end, the precipitate has to be left to settle for a considerable time after each addition; an additional function of the acetone is to prevent adsorption of the colour on the precipitate, making the latter a mauve colour and so masking the end-point. The phosphoric acid standard must be standardised against lead nitrate. The method was tested, with the following results:

(*a*) ***With Acetone.***

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0090	16·10	0·00907
0·0080	14·40	0·00812
0·0070	12·30	0·00694
0·0060	10·70	0·00603
0·0050	8·85	0·00499
0·0040	7·00	0·00395
0·0030	5·20	0·00293
0·0020	3·65	0·00206
0·0010	1·75	0·00099
0·0100	17·75	0·01002

The first nine of these results were calculated from the factor (1·0 ml. ≡ 0·0005645 g. of $Pb[NO_3]_2$) obtained by the tenth titration; the tenth result was calculated from the mean of the factors obtained from the other nine (1·0 ml. ≡ 0·0005640 g. of $Pb[NO_3]_2$).

(*b*) *Without Acetone.*

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0100	9·15	0·01006
0·0090	8·10	0·00891
0·0080	7·30	0·00802
0·0070	6·35	0·00698
0·0060	5·45	0·00600
0·0050	4·55	0·00500
0·0040	3·65	0·00401
0·0030	2·70	0·00297
0·0020	1·80	0·00198
0·0010	0·95	0·00104

For these determinations a stronger phosphoric acid solution was used whose factor was 1·0 ml. ≡ 0·00110 g. of $Pb(NO_3)_2$.

The precipitate formed in the course of titration appears to have the composition $PbO(Pb_3[PO_4]_2)_2$.

Titration with Ammonium Vanadate.—Lead can be titrated in the same manner with ammonium vanadate. The following results were obtained by the use of a solution containing 0·0184 g. of $NH_4VO_32H_2O$ in 1000 ml. (1·0 ml. ≡ 0·00008 g. of V).

Lead nitrate taken g.	Titration ml.	Lead nitrate found g.
0·0100	13·80	0·00998
0·0090	12·45	0·00900
0·0080	11·05	0·00799
0·0070	9·70	0·00701
0·0060	8·32	0·00601
0·0050	7·00	0·00506
0·0040	5·55	0·00401
0·0030	4·20	0·00304
0·0020	2·80	0·00202
0·0010	1·37	0·00099

The factor (1 ml. ≡ 0·000723 g. of $Pb[NO_3]_2$) was calculated from the mean of the first four results. The titration is somewhat sharper than with phosphate, but the composition of the precipitate does not appear to correspond with any simple relationship of Pb:V. Probably a mixture of meta- and ortho-vanadate is formed (*cf.* Calliere and Guiter's work).[15]

DETERMINATION OF ACID RADICLES.—Many acid radicles are precipitated by lead salts at or near the neutrality point. The difficulty in using these reactions volumetrically, apart from the lack of an internal indicator, is the tendency of lead to form basic salts, thus rendering the composition of the precipitate uncertain. The reagent proposed, besides being a good internal indicator, provides a very efficient buffer, thus keeping the *p*H value within narrow limits; consequently several volumetric processes of very fair accuracy have been evolved. The acids dealt with are the following:—molybdic, tungstic, vanadic, phosphoric and arsenic.

None of these acids, with the exception of vanadic, gives any marked colour with the reagent (molybdic acid gives a pale orange); consequently, if a solution of lead nitrate is run into a solution of one of their salts containing the reagent, no marked colour change takes place until the lead is in excess, when the liquid begins to turn red. The end-point is very similar to that of a titration with alkali, using phenolphthalein as indicator.

Molybdates.—The solution is neutralised with ammonia or nitric acid, as the case may be (it is desirable that it should be on the alkaline rather than the acid side), and diluted to 100 ml.; 10 ml. of the reagent and 30 ml. of *alcohol* are added. The mixture is titrated with lead nitrate solution (1 g. of $Pb[NO_3]_2$ made up to 1000 ml.) to the appearance of the first permanent pink flush. The lead solution should be standardised in the same way against ammonium molybdate. Tested in this manner on a solution of ammonium molybdate the method gave the following figures:

Molybdenum taken g.	Titration ml.	Titration (calc. from the 0·004 Mo. figure) ml.
0·0100	36·00	36·10
0·0050	18·05	18·06
0·0040	14·45	—
0·0030	10·80	10·84
0·0020	7·25	7·23

The titration results therefore are strictly proportional within the limits of experimental error; they are not quite comparable with those next to be cited, as an old lead nitrate solution, probably slightly concentrated, was used.

The process was tried on a sample of MoO_3 obtained in the course of a molybdenum determination. The sample, which weighed 0·0527 g. (this included the weight of the filter-ash) was dissolved in sodium hydroxide and made up to 250 ml.; portions were neutralised separately with nitric acid and titrated as described above.

	Volume taken ml.	Titration ml.	MoO_3 g.	Calculated total weight of MoO_3 g.
(*a*)	25·0	12·30	0·00519	0·0519
(*b*)	25·0	12·30	0·00519	0·0519
(*c*)	50·0	24·70	0·01042	0·0521
(*d*)	20·0	9·80	0·00414	0·0518
*(*e*)	10·0	5·00	0·00211	0·0527
(*f*)	10·0	4·90	0·00207	0·0518
(*g*)	10·0	4·95	0·00209	0·0522
(*h*)	10·0	4·95	0·00209	0·0522
†(*i*)	10·0	4·95	0·00209	0·0522

* Neutralisation rather too much on acid side.

† Faintly alkaline.

It will be noted that, leaving out of consideration (*e*), the neutralisation of which was at fault, the results group themselves closely round their mean 0·0520; the excess, 0·0007 g., is presumed to be the weight of the filter ash contained in the sample.

Details of the standardisation are as follows:

Molybdenum taken g.	Titration ml.	Titration (calc. to 0·010 g. of Mo) ml.	Mean ml.
0·0050	17·8	35·6	35·575
0·0040	14·2	35·5	
0·0030	10·7	35·7	
0·0020	7·1	35·5	

Hence 1·0 ml. ≡ 0·0004218 g. of MoO_3.

From the foregoing figures it appears that the reaction is not quite stoichiometric for the formula $PbMoO_4$

1 atom of Pb ≡ 1·03 instead of 1·00 atom of Mo.

Phosphates.—The following titrations were carried out on the phosphoric acid solution used for titrating lead (*vide supra*). In view of the very faint acidity of the solution, no neutralisation was attempted. The titration was performed in exactly the same manner as for molybdates, except that 30 ml. of acetone were used instead of 30 ml. of alcohol.

H_3PO_4 solution taken ml.	Titration, $Pb(NO_3)_2$ ml.	P_2O_5 found calc. from formula $PbO(Pb_3[PO_4]_2)_3$ g.	P_2O_5 present, calc. from NaOH filtration g.
10·0	6·9	0·000888	0·000898
5·0	3·5	0·000450	0·000449
4·0	2·8	0·000360	0·000359
3·0	2·2	0·000283	0·000274
2·0	1·5	0·000193	0·000180
1·0	0·7	0·000090	0·000090

It will be noted that the compound formed when lead nitrate is run into excess of phosphoric acid appears to be $PbO(Pb_3[PO_4]_2)_3$ instead of the $PbO(Pb_3[PO_4]_2)_2$ formed when the phosphoric acid is run into excess of lead.

Arsenates.—The following titrations were carried out exactly as for phosphates; the solutions titrated were very slightly on the alkaline side of neutrality.

As^v taken g.	Titration ml.	Calc. factor 0·001 As^v ≡ $Pb(NO_3)_2$ g.	As^v found, calc. from mean factor g.
0·00100	7·5	0·0075	0·001000
0·00080	6·0	0·0075	0·000800
0·00060	4·5	0·0073	0·000600
0·00050	3·8	0·0076	0·000506
0·00040	3·0	0·0075	0·000400
0·00030	2·3	0·0077	0·000308
0·00020	1·5	0·0075	0·000200
0·00010	0·75	0·0075	0·000100

Mean 0·0075

The atomic ratio $\mathrm{As^{V}}$:Pb, calculated from the mean factor, is 1:1·70, which lies about half-way between the two ratios given for phosphates (4:7 and 6:10 *vide supra*). Arsenites do not appear to influence the titration.

Vanadates.—The acids so far dealt with give little or no colour with the reagent; with vanadium this is not so. $\mathrm{Vanadium^{V}}$ gives a colour almost identical with that of lead, $\mathrm{V^{iv}}$ gives a very intense violet; in a titration with lead $\mathrm{V^{iv}}$ does not come into consideration, but it will obviously be necessary to ensure that all vanadium is in the highest stage of oxidation. If a neutral solution of a vanadate to which the reagent has been added is titrated with lead nitrate solution the cherry-red colour of the $\mathrm{V^{V}}$ fades as lead vanadate is precipitated till only the colour of the reagent itself is left; an excess of lead then causes the lead colour to appear. The titration is therefore very easy to perform; it is carried out in exactly the same way as that for phosphates (*i.e.* neutral solution, volume 100 ml., 10 ml. of reagent and 30 ml. of acetone).

A series of titrations carried out on ammonium vanadate gave the following results:

			$\mathrm{Vanadium^{V}}$ found	
$\mathrm{Vanadium^{V}}$ taken g.	Titration ml.	Factor calc. from result 0·001 V ≡ ml. $Pb(NO_3)_2$	Calc. from mean of factors 0·0008 – 0·00056	Calc. from formula $3PbO[Pb(VO_3)_2]_2$
0·00160	12·40	7·75	0·001544	0·001527
0·00120	9·40	7·84	0·001171	0·001158
0·00080	6·40	8·00	0·000797	0·000788
0·00072	5·80	8·05	0·000722	0·000714
0·00064	5·15	8·05	0·000641	0·000634
0·00056	4·50	8·04	0·000560	0·000554
0·00048	3·90	8·12	0·000485	0·000480
0·00040	3·20	8·00	0·000398	0·000394
0·00032	2·60	8·12	0·000324	0·000320
0·00024	1·95	8·12	0·000243	0·000240
0·00016	1·25	7·81	0·000156	0·000154
0·00008	0·65	8·12	0·000081	0·000080

It will be noted that results above 0·001 g. tend to be low, although those below that amount show very good agreement; for this reason the method is not recommended for amounts of vanadium in excess of 0·001 g. Hence the factor from which the results in column 4 were calculated was the mean of the first four within the accepted range (those enclosed in brackets); this factor is 1·0 ml. ≡ 0·0001245 g. of V; from this the atomic ratio of V: Pb in the precipitate can be deduced, giving 1:1·236, roughly corresponding to $3(PbO)(Pb[VO_3]_2)_2$, which requires an atomic ratio of 1:1·25 and gives a factor of 1 ml. ≡ 0·0001232, or possibly a mixture of meta- and ortho-vanadate is formed (*vide supra*). A paper has recently been published (ANALYST, 1938, **63**, 870) in which is described a volumetric method for determining amounts of vanadium from 0·01 to 0·001 g., covering the interval between this method and the ordinary permanganate process. The whole range of amounts of vanadium down to below 0·08 mg. can therefore now be determined volumetrically. When it is remembered that 0·2 mg. of vanadium gives only a very faint, and 0·1 mg. an almost imperceptible, colour with hydrogen peroxide in the ordinary colorimetric process[5] the significance of the process just described becomes apparent.

Tungstates.—The last member of the series of acids under consideration is exceedingly difficult to determine in small amounts. We are not here concerned with its separation from other elements (*cf.* Schoeller,[6] Yagoda and Fales,[7] Halberstadt[8]); the present research was undertaken primarily to provide the necessary step of an accurate means of determining the small amount when separated. Lead tungstate is precipitated very completely from neutral solution, but it readily dissolves in either acid or alkali; from pyridine-buffered solution, however, precipitation appears to be as complete as one could wish. It seemed obvious that, if the constitution of the precipitated lead tungstate could be regulated, the method of titration already described for phosphates, etc., should be available also for tungstates. The first experiments were made by adding a known excess of lead nitrate to the buffered solution and titrating the excess of lead away with phosphoric acid, as described already. The results obtained were only approximate and tended to be high (*i.e.* they were not very consistent among themselves and an excess of lead over that required by the formula $PbWO_4$ was used up). Apparently, basic compounds (or adsorption complexes) were being precipitated and these, as might be expected with tungsten, were of uncertain composition; it was felt that with this particular element an attempt must be made to produce a precipitate of the theoretical composition, $PbWO_4$. After many experiments it was found that the addition of boric acid seemed to prevent the adsorption of lead (basic compounds did not appear to be formed); in fact, too much boric acid swung the results over slightly in the opposite direction. The following figures illustrate this effect:

Tungsten taken g.	Boric acid added, saturated solution ml.	Titration, standard $Pb(NO_3)_2$ ml.	Tungsten found, calc. from formula $PbWO_4$ g.
0·003	nil	20·00 − 13·95 = 6·05	0·00336
0·003	10	10·00 − 4·82 = 5·18	0·00288
0·003	10	11·00 − 5·80 = 5·20	0·00289
0·003	5	10·00 − 4·82 = 5·18	0·00288
0·003	2	10·00 − 4·65 = 5·35	0·00297

A series of titrations was accordingly made in which 2 ml. of saturated boric acid solution were added to the neutralised tungstate solution diluted to such a volume that, with the lead nitrate solution to be added, the volume would be about 100 ml., the excess of standard lead nitrate was next run in, followed by 10 ml. of the reagent and 30 ml. of acetone; the excess of lead was then titrated with standard phosphoric acid exactly as described at the beginning of this paper. The following figures were obtained:

		Titration,					
Tungsten taken g.	H_3PO_4 ml.	$Pb(NO_3)_2$ solution added ml.		$Pb(NO_3)_2$ solution equiv. to H_3PO_4 ml.		$Pb(NO_3)_2$ solution required for WO_3 ml.	Tungsten found, calc. from $PbWO_4$ formula g.
0·0100	2·40	20·00	−	2·12	=	17·88	0·00994
0·0090	4·15	20·00	−	3·67	=	16·33	0·00907
0·0080	1·00	15·00	−	0·88	=	14·12	0·00785
0·0070	2·80	15·00	−	2·48	=	12·52	0·00696
0·0060	4·70	15·00	−	4·16	=	10·84	0·00602
0·0050	6·60	15·00	−	5·85	=	9·15	0·00508
0·0040	3·15	10·00	−	2·79	=	7·21	0·00401
0·0030	5·25	10·00	−	4·65	=	5·35	0·00297
0·0020	1·45	5·00	−	1·28	=	3·72	0·00207
0·0010	3·65	5·00	−	3·23	=	1·77	0·00098

Standardisation: 1 ml. of H_3PO_4 solution $\equiv$ 0·885 ml. of $Pb(NO_3)_2$ solution.

Repeated attempts to filter out the lead tungstate before titration invariably gave high results. It would seem that lead is withdrawn as a loose adsorption complex which is broken down during the titration.

Some titrations were also carried out on amounts of tungsten unknown to the operator. The results were as follows:

		Titration,					
Tungsten given g.	H_3PO_4 ml.	$Pb(NO_3)_2$ solution added ml.		$Pb(NO_3)_2$ solution equiv. to H_3PO_4 ml.		$Pb(NO_3)_2$ solution required for WO_3 ml.	Tungsten found, calc. from $PbWO_4$ formula g.
0·00370	15·05	20·00	−	13·32	=	6·68	0·00371
0·00610	10·50	20·00	−	9·12	=	10·88	0·00604
0·00550	11·40	20·00	−	10·09	=	9·91	0·00551
0·00085	21·10	20·00	−	18·67	=	1·33	0·00074
0·00122	20·20	20·00	−	17·90	=	2·10	0·00117
0·00188	19·00	20·00	−	16·80	=	3·20	0·00178

Standardisation: 1 ml. of H_3PO_4 solution $\equiv$ 0·85 ml. of $Pb(NO_3)_2$ solution.

The foregoing work was carried out before the direct titration process for phosphates, etc., was discovered (*vide supra*); it seemed worth while therefore to ascertain if this process was also available for tungstates. The titration was performed in the manner described for vanadium, but 40 ml. of acetone, instead of 30, were added; as the end-point was rather difficult to observe 1 ml. of the lead nitrate standard was added to a blank and the tungsten solution was titrated until the colours matched, 1 ml. being deducted from the result. The following results were obtained:

Tungsten taken g.	Titration ($Pb[NO_3]_2$) solution ml.	Tungsten found, calc. from $PbWO_4$ formula g.
0·0100	18·9−1·0=17·9	0·00995
0·0050	10·0−1·0= 9·0	0·00500
0·0040	8·3−1·0= 7·3	0·00405
0·0030	6·4−1·0= 5·4	0·00300
0·0020	4·6−1·0= 3·6	0·00200
0·0010	2·9−1·0= 1·9	0·00106
Unknown to operator		
0·0041	8·0−1·0= 7·0	0·0039

Owing to the production of a slight mauve tint, due presumably to adsorption of the lead colour on the precipitate, it is as well to allow the vessel to stand for a few minutes before the final matching.

Somewhat contrary to expectation, therefore, tungstic acid alone amongst the acids dealt with appears to throw down the normal lead salt. The addition of acetone is more important in titrations of tungstates than of the other acids, as without it the lead colour is adsorbed on the lead tungstate, making the end-point very difficult to observe.

OTHER VOLUMETRIC METHODS FOR TUNGSTEN.—A paper published in 1936[11] contains an account of various diamine scarlets used as indicators for lead in a lead-tungstate titration somewhat similar to that given here. The dyes act as adsorption indicators, and the results given are excellent, but the quantities dealt with are not as small nor as varied as those which form the subject of this paper; also, titration has to be carried out at the boiling-point. Another published volumetric method for tungsten appears to rely on some form of acidimetry.[12]

Dotreppe's reduction method[13] has been severely criticised by Holt.[14]

NEUTRALISATION.—In view of the fact that carbonates seem to act in the same way as phosphates, etc., in destroying the lead colour which is the subject of this paper, it is necessary to bear in mind their possible introduction during neutralisation. For this reason it is best to boil the solution, neutralised with sodium hydroxide, and then make faintly acid with nitric acid, and, after cooling, to bring it back to neutrality or faint alkalinity by cautious addition of dilute ammonia (*not* sodium hydroxide solution). The exact *p*H value does not matter very much except where tungstates are being titrated, as then the colour is being matched and the intensity of the colour is extremely sensitive to *p*H value. In this instance it is best to add 10 ml. of 20 per cent. ammonium nitrate solution to both the sample and the blank (the latter must not be omitted because ammonium nitrate distinctly lightens the colour) before adding the reagent. The titration of tungstates is being investigated further.

OTHER ACIDS.—The titration should theoretically work with chromates, but when this was tried a dark brown colour developed during the titration and entirely obscured the end-point. Many organic acids (*e.g.* citric) are precipitated by lead in neutral solution, and the titration should undoubtedly be available for them. In all the work hitherto described the strength of the titrating solution was 1·00 g. of lead nitrate per 1000 ml. It is desirable always to standardise it against the particular ion to be titrated and to use the same batch of reagent.

BEHAVIOUR OF THE REAGENT WITH DIFFERENT IONS.—The reagent gives colours with a number of ions; its behaviour is summarised in the following table:

ION	REACTION
Cu^{II}	Red colour immediately fading and replaced by the pyridine blue colour.
Cr^{VI}	No effect.
Cr^{III}	No effect.
Fe^{III}	$Fe(OH)_3$ precipitated; no colour.
Fe^{II}	Red colour.
Hg^{II}	Intense violet colour.
Hg^{I}	Intense violet colour.
Zn^{II}	Purple red colour tending to precipitate.
Co^{II}	Purple red colour tending to precipitate.
Ni^{II}	Purple red colour tending to precipitate.
Pb^{II}	Red colour.
Cd^{II}	Red colour.
Mn^{II}	Slight reddish brown (impurity ?).
V^{V}	Red colour.
V^{IV}	Intense violet colour.
W^{VI}	No effect.
Ti^{IV}	No effect.
Mo^{VI}	Pale orange brown.
U^{VI}	Slight yellow colour.
Sn^{II}	Red colour.
Sn^{IV}	No effect.
Tl^{I}	No effect.
Ag^{I}	Slight brownish-red.
Bi^{III}	Slight red colour (probably impurity).

Cl' SO_4'' NO_3' PO_4''' AsO_4''' AsO_3''' SO_3'' No action.

The red colour of vanadium^{v} is not interfered with by titanium^{iv}, which gives no colour itself. Citrates and tartrates appear to destroy the colour not only of the lead complex but of that of vanadium^{v} and vanadium^{iv} as well. Many of the coloured compounds, notably those of zinc, nickel and cobalt, are extractable with chloroform; that of lead seems to be partially and with difficulty extracted but slowly destroyed, the reagent passing into the chloroform. The action of copper (*vide supra*) appears to destroy the reagent, as the solution no longer gives a red colour with lead; copper must therefore be eliminated. Some of the colours are probably merely those given with carbazones.

It seemed worth while to attempt titrating away the colours of some of these cations in much the same way as was done for lead. Zinc and nickel were tried, but only with zinc was success achieved; the nickel complex seems to be too stable for its ready titration.

ZINC.—To obtain a satisfactory colour with this metal a rather higher pH is needed than for lead; consequently, if one attempts to form it in the same manner as with lead the appearance of the colour is somewhat uncertain. Chloroform appears to catalyse the formation of the coloured compound, which dissolves in it; this has the additional advantage of concentrating the colour and making the titration sharper.

The following process was tried:—The neutralised zinc solution was diluted to 100 ml., 30 ml. of acetone were added, followed by 5 ml. of the reagent, and lastly 5 ml. of chloroform; it was shaken and then titrated with $M/1000$ potassium ferrocyanide solution with vigorous shaking after each addition until the chloroform showed only the colour of the reagent. Results thus obtained were:

Zinc taken g.	Titration ($M/1000$ $K_4Fe[CN]_6$) ml.	Zinc found, calc. from the 0·001 Zn titration figure g.
0·0010	8·30	0·000997 (calc. from mean factor of the other results)
0·0005	4·10	0·000494
0·0004	3·35	0·000403
0·0003	2·50	0·000301
0·0002	1·70	0·000205
0·0001	0·85	0·000102

If the titration figures are calculated on the ordinary basis, on the assumption that $K_2Zn_3(Fe[CN]_6)_2$ is precipitated, the results are about 20 per cent. too low. The ratio Zn : $K_4Fe(CN)_6$ is approximately 2 atoms of Zn : 1 molecule of $K_4Fe(CN)_6$. Subsequent determinations have shown that if, in the neutralisation, an excess of pyridine is added to the faintly acid solution, the exact ratio is obtained and therefore the theoretical factor (1 ml. of $M/1000$ $K_4Fe(CN)_6 \equiv 0{\cdot}0001308$ Zn) for $Zn_2Fe(CN)_6$ can be used. The only modification required in the process described above is that neutralisation should be carried slightly to the acid side of neutrality, and 1 ml. of 20 per cent. pyridine should then be added.

It has since been found that minute traces of nickel are exceedingly liable to be introduced in the course of an analysis and that these entirely upset the titration by producing a pink colour which cannot be titrated away. This can be counteracted by adding 2 drops of 10 per cent. potassium cyanide solution immediately after the pyridine and allowing to stand for 2 or 3 minutes before adding the reagent. The titration should then be completed without delay, as the nickel colour tends to recur. The blank liquid is treated in the same manner.

PYRIDINE.—The question of the supply of pyridine for these experiments was one of some difficulty. Commercial pyridine is exceedingly impure and the reagent prepared from it gave no colour at all, but a white precipitate, with lead; other supplies of alleged "pure" pyridine gave a reagent which produced a lead colour that almost immediately faded. AnalaR grades of pyridine were not tried. Satisfactory samples were supplied by both Messrs. Hopkin & Williams and British Drug Houses, and doubtless the requirements could easily be met by any manufacturer who knew them. The interfering substances would seem to be ammonia or homologues or derivatives of pyridine; water apparently has no effect whatever. It was found that if commercial pyridine is distilled from lead nitrate and the distillate subsequently boiled for 10 minutes in an open vessel the product can be used to prepare a very fair reagent; it however does not keep nearly as long, and on the whole is not so satisfactory, as that made from Messrs. Hopkin & Williams' or the B.D.H. product. The use of other organic bases (*e.g.* cinchonine and aniline) is being investigated with fairly promising results up to the present.

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Quinaldinic Acid as a Reagent for Copper, Zinc and Cadmium

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QUINALDINIC acid has been proposed as an analytical reagent for the quantitative determination of a number of metals,[1,2,3,4,5] and has been recommended as being suitable for the separation of copper from cadmium.[1,4]. The following investigation was undertaken to establish the *p*H range over which complete precipitation could be effected for the metals copper, zinc and cadmium, and so to define more precisely the conditions for determination.

DETERMINATION OF COPPER.—Copper sulphate, AnalaR (15 g.) was dissolved in water and the solution was diluted to 2500 ml. The copper-content of this solution was determined by the sodium anthranilate[6] method (found: copper, 0·03842 g. per 25 ml.).

To 25 ml. of the standard copper solution were added 25 ml. of sodium acetate solution (5 g.), a measured quantity of glacial acetic acid, and water to make up 150 ml. The solution was boiled and 20 ml. of reagent solution (5 g. of sodium quinaldinate in 250 ml. of water) were added slowly. After 45 minutes the precipitate was collected on a No. 4 sintered glass crucible, and the filtrate was reserved for subsequent *p*H determination by means of a hydrogen electrode. The precipitate was washed well with water, dried at 125° C. and weighed. The results are given in Table I.

Complete precipitation was obtained over the *p*H range 2·5 to 6·96. Attempts to extend the range above *p*H 7 resulted in the precipitation of copper hydroxide. In the absence of sodium acetate it was found possible to attain *p*H values below 2 and to extend the range of copper precipitation to *p*H 1·5.

TABLE I

Copper taken in each Experiment = 38·42 mg.

Acetic acid ml.	*p*H	Wt. of ppt. mg.	Copper found mg.
125*	0·69	nil	nil
100*	0·93	131·5	19·66
40*	1·43	251·7	37·54
35*	2·20	257·0	38·43
100	2·05	124·4	18·61
75	2·34	210·8	31·52
50	2·60	255·7	38·23
5	3·59	257·2	38·46
0·05	5·69	256·8	38·41
nil	6·96	256·8	38·41

* No sodium acetate buffer used in these experiments.

DETERMINATION OF CADMIUM.—Cadmium sulphate, AnalaR (9·6 g.), was dissolved in water and the solution was diluted to 2 litres. The cadmium was determined with anthranilic acid[8] (found: cadmium 55·17 mg. per 25 ml.).

The procedure adopted for the cadmium determinations was identical with that employed for copper. The results are given in Table II.

TABLE II

Cadmium taken in each Experiment = 55·17 mg.

Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Cadmium found mg.
20	3·15	nil	nil
10	3·37	54·1	13·32
5	3·95	223·9	55·13
0·1	5·92	223·8	55·11
0·05	6·47	223·8	55·11
nil	6·82	223·9	55·13
0·05 2N NaOH	7·17	224·2	55·21

It will be observed that complete precipitation is obtained over the *p*H range 3·9 to 7·2.

DETERMINATION OF ZINC.—Zinc, AnalaR (2·7 g.), was dissolved in the minimum quantity of nitric acid; the solution was made just alkaline with sodium carbonate and then just acid with acetic acid and diluted to 2 litres. The zinc was determined by the method of Funk and Ditt.[8]

The method of precipitation, washing and drying of zinc quinaldinate was similar to that employed for copper and cadmium. The results, shown in Table III, indicate that complete precipitation occurs over the range *p*H 2·3 to 6·5.

The foregoing series of precipitations were also expressed graphically. The results show that copper-zinc separations are impossible by adjustment of *p*H, and that if any separation of copper from cadmium or of zinc from cadmium is possible it should be over the *p*H range 2·7 to 3·1. When sodium acetate buffer was employed it exerted a pronounced solubility effect; a parallel case is that of copper anthranilate.[7]

TABLE III

Zinc taken in each Experiment = 33·82 mg.

Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Zinc found mg.
100	1·72	nil	nil
75	1·96	145·7	22·27
50	2·10	207·8	31·77
25	2·30	221·7	33·89
10	2·75	221·6	33·88
5	3·09	221·2	33·82
1	3·52	221·6	33·88
nil	5·43	221·1	33·80
0·1 2*N* NaOH	6·45	221·6	33·88

Experiments to separate copper from cadmium and zinc from cadmium were made. The conditions of precipitation, washing and drying were essentially those employed in the separate determinations. The results are recorded in Table IV.

TABLE IV

Cadmium taken in each Experiment = 55·17 mg.

Zinc or copper taken mg.	Glacial acetic acid ml.	*p*H	Wt. of ppt. mg.	Corresponding to copper or zinc mg.
38·42 Cu.	30	3·11	268·8	40·20 Cu.
38·42 Cu.	40	2·93	262·0	39·18 Cu.
38·42 Cu.	48	2·69	259·0	38·74 Cu.
33·82 Zn.	25	2·85	240·0	36·70 Zn.
33·82 Zn.	30	2·60	239·1	36·56 Zn.
33·82 Zn.	40	2·30	235·9	36·07 Zn.

High results were obtained in all experiments owing to co-precipitation of cadmium quinaldinate. In the separation of copper from cadmium, co-precipitation varied from 0·8 to 4·5 per cent. over the *p*H range 2·7 to 3·1. In the separation of zinc from cadmium the results were inaccurate to the extent of 8 per cent.

It is to be concluded from these results that while quinaldinic acid offers a convenient, rapid and highly accurate method of determining copper, zinc or cadmium separately, it is unsuited for separation of these metals from one another.

In conclusion I should like to thank Dr. A. J. Lindsey for the interest he has shown in this work.

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THE SIR JOHN CASS TECHNICAL INSTITUTE
JEWRY STREET, LONDON, E.C.3

July, 1938

The Vitamin A and Vitamin D Contents of Butter: II. Seasonal Variation

BY H. WILKINSON, B.SC., PH.D.

(*Read at the Meeting, November 2, 1938*)

IN a previous paper from this Laboratory (Morgan and Pritchard[1]) on the vitamin A and D contents of butter, the assays of part of a series of Scottish butters were reported. This series has now been completed and the assay results, together with those on a series of Danish butters, form the basis of the present paper. The variation during the year in the vitamin A and D contents of butter was shown in the previous paper, but the data were incomplete in that the dietary regime of the cows supplying the butter was not known, and indeed in many cases the origin of the butter was also unknown. The present results are of interest in that in the Scottish series the rough feeding details and the origin and time of manufacture are known, whilst in the Danish series the time and place of manufacture are known, although no feeding details are available.

EXPERIMENTAL TECHNIQUE.—The vitamin A content of each butter was determined directly by means of the biological technique described by Morgan.[2]

The vitamin D content of some of the higher potency butters was determined directly on the butter. The method due to Morgan[3] was used. The basal vitamin D-free diet has been slightly modified as shown below:

	(Morgan)	New diet
Maize flakes (ground) ..	72	84
Meat meal (extracted) ..	5	12
Salt mixture	4	4
Wheat gluten	19	—

Where the vitamin D potency was expected to be very low, assays were made by means of the Bechdel-Hoppert alcohol-extraction method,[4] but it has been found that this method does not give complete extraction of the vitamin D, a finding supported by other workers.

Attempts were therefore made to determine the vitamin D content directly by incorporating the butter in the diet in place of part of the maize flakes. This method has proved satisfactory, and has been used towards the end of the series.

SCOTTISH BUTTERS.—Arrangements were made with a creamery in Ayrshire to send us a monthly sample of butter, representative of the churning during 48 hours, and dispatched to us as soon as possible. Details of the feeding practised by the farmers during the month represented by the sample were also sent to us.

The district in which the creamery is situated lies between Rothesay, Renfrew and Dumfries. To calculate the hours of sunshine daily at the farms mentioned in this study, the average of the average number of hours of sunshine daily for each of the three places, mentioned above, has been calculated and taken as representative of the district. The values used in the calculation have been obtained from the Weekly Weather Report, Volume LIII (Meteorological Office), for the period March 1st, 1936, to February 27th, 1937. These figures are shown graphically in Fig. 1.

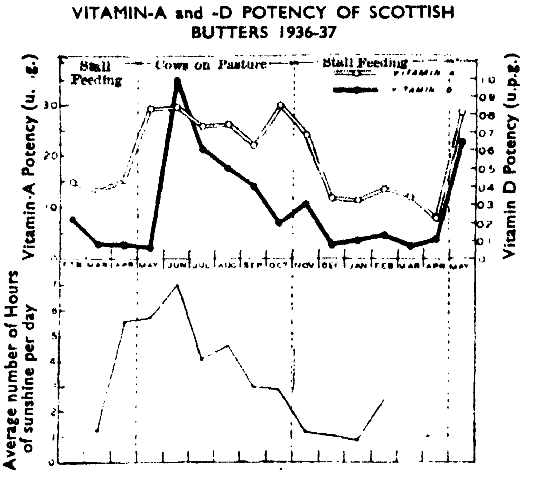

Fig. 1

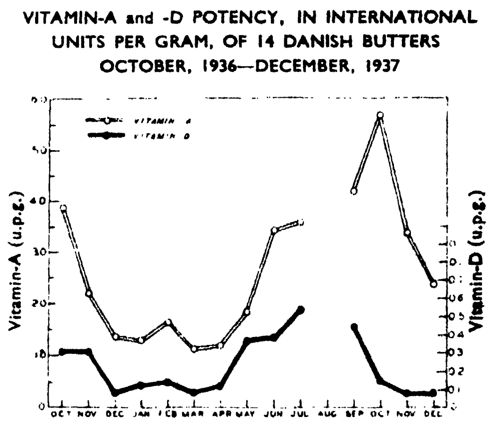

Fig. 2

The vitamin A and D contents of the butters are given in Table I, and shown in graphical form in Fig. 1. The feeding details are gathered together in Table II.

TABLE I

VITAMIN-A AND VITAMIN-D POTENCIES OF SCOTTISH BUTTERS, 1936/37

			Vitamin A (International units, per g. of butter)	Vitamin D (International units, per g. of butter)
February,	1936	..	14·8	0·22
March	,,	..	13·2	0·08
April	,,	i	15·3 } 15·3	0·07 } 0·08
		ii	15·3	0·08
May	,,	..	29·1	0·60
June	,,	..	29·5	0·99
July	,,	..	25·6	0·60
August	,,	..	26·0	0·50
September	,,	..	22·0	0·40
October	,,	..	29·9	0·20
November	,,	..	24·1	0·30
December	,,	..	11·8	0·08
January,	1937	..	11·4	0·11
February	,,	..	13·6	0·13
March	,,	..	12·2	0·08
April	,,	..	8·0	0·12
May	,,	..	28·6	0·65

TABLE II

The number of farms supplying milk to the creamery each month and the number of farms on which the different foodstuffs were fed during the month.

	1936										1937				
	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
Total No. of Farms	9	8	6	6	6	7	6	7	9	9	7	9	7	7	7
Grass	–	–	4	6	6	6	6	4	–	–	–	–	–	–	7
Concentrates ..	8	8	6	2	2	5	6	7	9	8	7	9	7	7	7
Straw	8	6	–	–	–	–	–	–	7	6	5	6	6	6	–
Hay	9	6	–	–	–	–	–	–	6	7	5	6	6	6	–
Turnips	3	1	–	–	–	–	–	–	4	6	3	4	5	2	–
Crushed oats	2	1	–	–	–	–	1	1	–	–	–	–	–	–	–
Beet pulp	4	5	–	–	–	–	–	–	3	3	3	4	2	4	–
Bean meal	1	–	–	–	–	–	–	–	3	3	3	4	3	2	–
Maize	1	–	–	–	–	–	–	–		–	–	1	–	–	–
Malt culms	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Lentil meal	1	–	–	–	–	–	–	–	1	1	1	1	1	1	–
Barley meal	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Screw pressed G.N.O. cake	1	–	–	–	–	–	–	–	–	–	–	–	–	–	
Cabbage	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–
Green cut hay ..	–	2	–	–	–	–	–	–	1	1	1	1	1	–	–
Potatoes	1	–	–	–	–	–	1	1	1	1	1	1	2	–	–
Marrow stem kale ..	–	–	–	–	–	1	1	3	4	–	–	–	–	–	–

DISCUSSION.—*Vitamin A.*—The highest and lowest vitamin A potencies encountered in this study are 29·9 u.p.g. in October, 1936, and 8·0 u.p.g. in April, 1937, respectively. The average vitamin A potency during the summer months, when the animals received grass, is 27·2 u.p.g., and the winter level is 13·8 u.p.g. The average value of the 16 samples assayed is 19·7 units of vitamin A per g. This value does not differ significantly from the average value reported by Morgan and Pritchard.[1] The seasonal variation, reported previously by many workers, is amply confirmed.

It is evident that the vitamin A content of these butters undergoes a considerable increase immediately after the beginning of pasture feeding. The high level reached in June falls away in July, August, and September, probably owing to deterioration in the quality of the pasture. However, in October there is obtained a significantly increased vitamin A potency, compared with the two previous months. This is due most probably to the flush of young grass that would occur in the pasture at that period. This rise in the vitamin A potency of butter has been reported before.[1] The cattle were taken from pasture at the end of October, and the November sample shows an immediate and rapid fall, which is continued through to December. This sample possesses about the normal vitamin A potency of winter butter. In 1937 there is again shown the sudden and rapid rise in the vitamin A potency of the butter when the cows go out to grass.

In Table II are given the rough feeding details, and various indications may be obtained from them:

(i) Only during grass feeding is the vitamin A potency of the butter significantly increased.

(ii) Although the peak in the vitamin A potency occurred in October, only 4 out of 7 farms were feeding grass, whilst in September all farms had their cows on pasture. The most probable explanation is that in October there occurs a flush of young grass in the pasture, coupled with the feeding on the other 3 farms of marrow stem kale and green-cut hay, both probably richer in carotene than the grass obtainable in September. The high value in November is due possibly to the feeding, on 4 farms, of marrow stem kale.

(iii) The winter feed is noticeably deficient in carotene, the precursor of vitamin A. This applies especially to all materials except the concentrates, the carotene and vitamin A contents of which are not known, and the green-cut hay.

Definite conclusions are difficult to draw, since the amounts fed per cow, the milk yield, and the amount of milk supplied to the creamery by each farm are unknown. However, the effects of the feeding regime are well demonstrated.

Vitamin D.—The variations in the vitamin D content of this series of Scottish butters are perhaps even more profound than the vitamin A variations. The highest potency was obtained in the June, 1936, sample (0·99 unit of vitamin D per g.), and the lowest of 0·08 u.p.g. in March, April and December, 1936, and March, 1937. The average summer value (*i.e.* while cows are out on grass) is 0·56 u.p.g., and the average winter value is 0·13 u.p.g. The average vitamin D content for the 16 samples is 0·32 u.p.g.

Consideration of Fig. 1 demonstrates quite clearly that the influence of the food on the vitamin D potency of the butter is negligible; the fall away is almost as rapid as the rise in potency, although almost the same feeding regime was practised for a further 4 months after the peak in June.

Campion *et al.*[5] have demonstrated that the vitamin D potency of butter varies directly with the amount of solar radiation which the cow receives. For this reason the approximate number of hours of sunshine per day have been calculated for the district around the farms supplying the milk. In Fig. 1 these values are shown graphically. The following points are of interest:

(i) Although the hours of sunshine in April and May in 1936 were high, the vitamin D potency of the butter was low. The reason for the low April sample is that the cows were being stall-fed (*i.e.* indoors) during this month and did not go out to grass until the beginning of May. It is most probable that the increase in vitamin D potency of the butter lags behind the beginning of the solar radiation, and this possibly accounts for the low vitamin D content of the May sample. The rapid increase in the May sample 1937 is due to the animals going out to grass about a fortnight earlier than in 1936.

(ii) The peak of the vitamin D potency in 1936 corresponds with the maximum number of hours of sunshine per day.

(iii) The falling away in the vitamin D potency is very closely related to the drop in the number of hours of sunshine per day.

It may be concluded, therefore, in confirmation of the results of Campion *et al.*,[8] that the vitamin D content of milk is due almost entirely to the ultra-violet irradiation that the cows receive.

DANISH BUTTERS.—These are authoritative samples representative of Danish butter churned in the Jutland district of Denmark. No data about feeding, or hours of sunshine, are available.

The vitamin A and D potencies are collected together in Table III and shown graphically in Fig. 2.

TABLE III

VITAMIN-A AND VITAMIN-D CONTENT OF DANISH BUTTER

Date			Vitamin A (International units, per g. of butter)	Vitamin D (International units, per g. of butter)
October,	1936	..	38·8	0·3
November	,,	..	22·0	0·3
December	,,	..	13·4	0·08
January,	1937	..	12·7	0·12
February	,,	..	16·9	0·14
March	,,	..	10·8	0·08
April	,,	..	11·7	0·12
May	,,	..	18·4	0·36
June	,,	..	34·2	0·38
July	,,	..	36·1	0·54
August	,,	..	—	—
September	,,	..	41·8	0·44
October	,,	..	56·7	0·15
November	,,	..	33·8	0·08
December	,,	..	23·7	0·08

DISCUSSION.—*Vitamin A.*—The vitamin A content of this series of butters varies more widely than that of the Scottish butters. The highest potency was found in the October 1937 sample, with 56·7 u.p.g. of butter. Incidentally, this is by far the highest potency that has been obtained for butter in this laboratory, the next highest being 41·8 u.p.g. shown in the previous month's sample (September, 1937). The lowest potency (10·8 u.p.g.) was shown in the sample of March, 1937. The average winter vitamin A potency is 18·1 u.p.g. (8 samples), which is higher than that reported for the Scottish butters (13·8 u.p.g.). This is due to the very high potencies of the last 2 samples received in November and December, 1937. The average vitamin A potency of the 14 samples is 26·5 u.p.g., which is higher than the averages of the 16 samples of Scottish butter described earlier in this paper and of the 75 samples of various butters described by Morgan and Pritchard.[1]

No feeding details are available, so that discussion of the results from this angle is impossible. The rise in potency in October, noted previously in our work on butter, has been obtained, but unfortunately the August sample was not received, so that it is not possible to tell whether there was a fall in potency in September before the October increase. However, the general trend of the results follows previous experience.

Vitamin D.—A variation in vitamin D content similar to that previously reported has been obtained in this series of butters. The range, however, is not as wide as in the Scottish butters, the lowest level being the same (0·08 u.p.g. in December, 1936 and 1937, March and November, 1937), but the highest level (0·54 u.p.g.) is only about half the highest Scottish level, and is reached in July, 1937. The amount of sunshine may, of course, have been less in Jutland in 1937 than in Scotland in 1936. The average winter level is 0·12 u.p.g., and the summer level 0·36, with an average over the year (14 samples) of 0·23 u.p.g.

Calculation of Errors*.—Each assay is calculated from the mean of the "pair differences." The standard deviation (σ) of the pair differences of each assay is given by:

$$\sigma = \sqrt{\frac{\Sigma(x - M)^2}{n - 1}},$$

where x = a pair difference, n = number of pairs, M = mean,

the limits on either side of the mean within which two-thirds of the pair differences could be expected to lie being given by $M \pm 6$.

Similarly, the standard deviation of a group of m assays will be:

$$\sqrt{\frac{\Sigma\Sigma(x - M)^2}{N - m}}$$

where N = total number of pair differences ($= \Sigma n$)

This value can be used to estimate the "probable error" *of the assays themselves, i.e.* the percentage limits of the assay within which there is 1 chance in 2 that the true assay lies, by combining it with the growth/dosage equation in the case of the vitamin A tests and the healing/dosage equation in the case of the vitamin D tests.

Besides the probable error (P.E.), two other standards are in common use, *viz.* 2 × P.E., which gives the limits within which there are 21 in 22 chances of truth, and 2·576 × P.E., which gives the limits of 99 in 100 chances. This latter error, written usually as "limits of error (P = 0·99)," has been adopted in the British Pharmacopoeia Addendum, 1936.

All three methods of expression are given below for the four groups of assays. Although the average number of pairs used per test was 9, the errors have been calculated on 10 pairs, this being the standard number.

TABLE IV

PERCENTAGE ERROR

WITH 10 PAIRS OF RATS PER TEST

Vitamin-A Assays

	Scottish butters		Danish butters	
P.E.	+7	−6	+7	−7
3 P.E.	+21	−17	+24	−19
P = 0·99	+28	−22	+31	−24

Vitamin-D Assays

	Scottish butters		Danish butters	
P.E.	+9	−8	+9	−8
3 P.E.	+29	−22	+28	−22
P = 0·99	+39	−28	+38	−27

Cf.* Coward, ANALYST, 1934, **59, 681.

For biological tests, these errors may be considered very satisfactory. They are considerably smaller than the representative "limits of error (P = 0·99)" quoted by the B.P. Addendum, which are:

For vitamin A assays (10 pairs) + 239 per cent. − 70 per cent.
" " D " (10 ") + 115 " " − 51 " "

SUMMARY.—Two series of butters taken at monthly intervals, one in Scotland and the other in Denmark, have been assayed for vitamin A and vitamin D. The typical monthly variation is shown in both series, the highest vitamin A value being obtained when the cows are on grass. One sample (October, 1937) in the Danish butter series has a vitamin A potency of 56·7 u.p.g., which is the highest potency recorded in this laboratory.

The variation in the vitamin D potency of the Scottish butters has been related to the variation in the amount of sunshine received by the cows on pasture. It has not been possible to do this for the Danish butters owing to lack of the necessary data.

The percentage error of the assays has been calculated.

I wish to thank the directors of Lever Brothers & Unilever, Ltd., for permission to publish these results.

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FOOD RESEARCH LABORATORY
LEVER BROS. & UNILEVER, LTD.
PORT SUNLIGHT

May, 1938

The Determination of Cobalt in Animal Tissues

BY K. J. McNAUGHT, M.Sc.

(*Read at the Meeting, October* 5, 1938)

THE importance that cobalt has assumed in recent years in the treatment of certain types of wasting disease in sheep and cattle, in Western and South Australia,[1,2] in different parts of New Zealand,[3,4] and in Florida,[5] has focussed attention on the determination of the very small amounts of this element normally present in animal tissues.

Bertrand *et al.*,[6,7] using α-nitroso β-naphthol reagent, succeeded in determining the cobalt content of various animal organs and tissues, but their method requires very large amounts of material. Stare and Elvehjem,[8] using Van Klooster's nitroso-R-salt reagent, developed a colorimetric method sensitive to 0·01 mg. of cobalt, but were unable to demonstrate the presence of this element in the bodies of normal rats and pigs.

The nitroso-R-salt reagent is, however, much more sensitive than the work of Stare and Elvehjem would indicate. A modification of their method that I made[9] was found applicable to rat tissues,[10] with as little as 0·0002 mg. of cobalt available for the determination. By still further refinement, a method sensitive to 0·00005 mg. of cobalt has been attained, making possible the investigation of this element in "bush-sick" pastures in New Zealand,[11] and in various animal organs.[12,13]

For animal tissues experience has shown that a modified nitric and sulphuric acid digestion method, which has been generally used for toxicological work in this laboratory for several years past, is preferable to ashing. The method is detailed below:

REAGENTS USED.—(1) Conc. nitric acid distilled from glass. (2) Conc. sulphuric acid of analytical reagent quality. (3) Hydrochloric acid of constant b.p., distilled from glass. (4) Ether of analytical reagent quality. (5) Hydrated sodium acetate (analytical reagent quality). (6) A 0·2 per cent. solution of phenolphthalein in 50 per cent. alcohol. (7) Potassium hydroxide of analytical reagent quality (about 30 per cent. solution). (8) A 0·1 per cent. solution of nitroso-R-salt. (9) Cobalt chloride of analytical reagent quality (0·4037 g. of $CoCl_2.6H_2O$ per litre gives a standard containing 0·1 mg. of cobalt per ml.).

PREPARATION OF THE TEST SOLUTION.—The sample (10 g. of dry tissue may conveniently be used) is moistened with about 20 ml. of water and 10 ml. of nitric acid, and the mixture is gently boiled. The flame temperature is raised and the boiling continued to reduce the volume to about 15 ml. The resulting partly digested mixture is allowed to cool for several minutes and 20 ml. of sulphuric acid are added. A rather vigorous reaction, with evolution of nitrous fumes, usually ensues and the solution finally chars. It is allowed to cool for a further few minutes, a few ml. of nitric acid are added, and the solution is heated, gently at first, but gradually more strongly, until the brown fumes cease and further charring begins. The nitric acid treatment is repeated until the solution, after being heated until white fumes have appeared, and then cooled, is quite colourless.

This digestion process can be conveniently completed in three to six hours, depending on the amount and nature of the sample being analysed, whereas digestion in the normal way with addition of the sulphuric acid at the initial stage is a much more prolonged process owing to the intense charring that results. The method has the further advantage that frothing is avoided, and, provided that the solution is allowed to cool sufficiently before the addition of further amounts of nitric acid, the consumption of this acid is greatly reduced (for 10 g. of dried liver the average requirement is about 40 ml.).

The sulphuric acid is driven off in a basin over an Argand burner, and the residue is heated for five minutes in the muffle furnace at 500° C. to destroy any residual traces of organic matter. The residue is taken up on the steam-bath with hydrochloric acid of constant b.p. Most of the iron is removed from such a solution by shaking with successive portions of ether until the ethereal layer is no longer yellow, and copper is removed by means of hydrogen sulphide. The dissolved hydrogen sulphide is expelled, a few drops of strong nitric acid are added, and the solution is evaporated just to dryness on the steam-bath. The residue is taken up in about 15 ml. of water on the steam-bath, and the resulting solution is transferred to a 50-ml. beaker and evaporated to about 7 to 8 ml.; it is then ready for the determination of cobalt.*

DETERMINATION OF THE COBALT.—One g. of sodium acetate and a drop of phenolphthalein indicator are added. The solution is warmed and treated with strong potassium hydroxide solution until the reaction is just alkaline, and then diluted with hydrochloric acid to make it faintly acid again. One ml. of a 0·1 per cent. solution of nitroso-R-salt is added and the solution is boiled for half-a-minute. To the boiling solution 1·5 ml. of conc. nitric acid is added, drop by drop, with constant stirring. The rate of addition should not exceed one drop per second and the boiling should be continued for a further half-minute after the acid has been added. The solution is allowed to cool for half-an-hour, protected from sunlight, and then made up to 10 ml. and matched in 10-ml. narrow graduated tubes (14 cm. deep by less than 1 cm. in diameter) against standards developed in the same way. If the volumes and conditions of the standard and test solutions are kept as nearly alike as possible, very satisfactory matching of the colours may be attained with amounts down to 0·05γ of cobalt or even less.

The refinements introduced in this modification of the Stare and Elvehjem method for the determination of cobalt are as follows:

(1) Precautions in preparation of the test solution to ensure the absence of interfering substances. Copper and iron in amounts up to 100γ and 1000γ, respectively, do not interfere with the determination of 1γ of cobalt in such solutions.

(2) Neutralisation of the solution before addition of the nitroso-R-salt. As the reagent is highly coloured, the neutralisation of the solution is usually difficult in its presence and large amounts of phenolphthalein indicator may be required. Furthermore, although the final cobalt complex with nitroso-R-salt is very stable to boiling nitric acid, the reagent itself is readily attacked in hot acid solution by oxidising agents and even by mild reducing agents, such as citric acid.[9] Neutralisation before addition of the reagent avoids any such difficulty.

(3) Reduction in the amount of reagent used.

(4) Reduction in the final volume of the solution to 10 ml.

(5) Use of special deep tubes of narrow bore for the colour matching.

Another modification[14,15] of the Stare and Elvehjem method, claimed to be sensitive to 0·0001 mg., has been described, but in this method the objectionable practice of adding the reagent before neutralisation has been retained.

The sensitivity of the present method is shown by the analysis of individual rat livers (Table I).

These results may be compared with a value of 0·14 p.p.m. obtained previously from the analysis of a composite sample of seven normal rat livers.[13]

The reliability of the above figures is indicated by recoveries of cobalt (0·2γ)

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* This wet digestion process was thought at the time to be novel, but it has since been found that the essential procedure of the preliminary treatment with nitric acid before the addition of sulphuric acid is similar to that described in the First Report of the Sub-Committee on the Determination of Arsenic Lead and other Poisonous Metals in Food Colouring Materials (ANALYST, 1930, 55, 107).—K. J. McN.

TABLE I

COBALT (Co) IN LIVERS OF NORMAL RATS

Sample No.	Total weights Wet wt. g.	Total weights Dry wt. g.	Taken for analysis Dry wt. g.	Co found mg.	Co found p.p.m. on dry weight
1	3·782	1·079	0·768	0·00017	0·22
2	3·146	0·913	0·644	0·00013	0·20
3	3·177	0·904	0·646	0·00014	0·22
4	4·321	1·244	0·918	0·00018	0·20
5	3·875	1·135	0·832	0·00014	0·17
6	3·871	1·054	0·770	0·00018	0·24
7	3·440	0·965	0·712	0·00012	0·17
				Average	0·20

added to a similar weight of a sample of dried sheep liver of approximately the same cobalt-content (Table II).

TABLE II

RECOVERIES OF COBALT (Co)

Weight taken g.	Cobalt added mg.	Cobalt found mg.		Recoveries Per Cent.
1·00	—	0·00024	Av. 0·00022*	—
,,	—	0·00020		—
,,	—	0·00022		—
,,	0·00020	0·00040		90
,,	,,	0·00043		105
,,	,,	0·00041		95
			Average	97

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* Duplicate analyses of 10-g. samples gave an average value in exact agreement with this figure (0·22 p.p.m.). The much lower cobalt-content of the livers of sheep and cattle suffering from cobalt deficiency (about 0·01 to 0·06 p.p.m.) necessitates the digestion of a larger amount of tissue.

SUMMARY.—(1) A rapid and convenient method for the wet digestion of animal tissue, involving preliminary treatment with nitric acid before the addition of sulphuric acid, and avoiding intense charring, is described.

(2) A delicate method sensitive to 0·05γ for the determination of cobalt is detailed and illustrated by the analysis of individual liver samples from some normal rats.

(3) With the procedure described good recoveries of added cobalt are obtained.

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13. S. W. Josland and K. J. McNaught, *Id.*, 1938, **19**, 536.
14. E. B. Kidson, H. O. Askew and J. K. Dixon, *Id.*, 1936, **18**, 601.
15. H. O. Askew and J. K. Dixon, *Id.*, 1937, **18**, 707.

CHEMISTRY SECTION
DEPARTMENT OF AGRICULTURE
WELLINGTON, NEW ZEALAND

August 9, 1938

Erratum.—December issue, p. 869: *For* "Present-day fertilisers contain very little chloride," *read* "Present-day fertilisers containing nitrate contain very little chloride."

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THALLOUS CARBONATE AS A STANDARD IN VOLUMETRIC ANALYSIS

THE requirements of a suitable standard for volumetric work may be stated very briefly. The substance should be readily obtainable in a high degree of purity, it should have a high equivalent weight, and it should be of such a nature as to be weighable with certainty. On this account hygroscopic substances and substances that contain water of crystallisation are to be avoided. Substances that can react both as acids and as oxidising agents have certain obvious advantages. Potassium bi-iodate can be obtained in a high degree of purity, and it enables acidimetric and iodimetric determinations to be correlated. Similar considerations apply to potassium quadroxalate, which can serve as a standard for permanganate as well as for alkalis. Potassium quadroxalate, however, crystallises with two molecular proportions of water, and may be open to objection on that account.

So far as I am aware, the claims of thallous carbonate have not yet received the attention they deserve. This compound was first prepared by Crookes and by Lamy more than seventy years ago, and it appears to have received little study since that time. The compound is easily prepared by saturating a solution of thallous hydroxide with carbon dioxide. Crookes made a few determinations of its solubility, and found that 100 parts of water dissolved 4·2 parts of the salt at 15·5° C. and 27·2 parts at 100° C. Similar figures were published about the same time by Lamy. The compound is readily obtained in highly pure condition by recrystallisation from water which must contain excess of carbon dioxide to suppress hydrolysis.

Preparation of Thallous Carbonate.—Granulated thallium was covered with water and gradually converted into a solution of thallous hydroxide by aspirating air through the solution. The solution was then filtered and saturated with carbon dioxide. Thallous carbonate crystallised out, but after prolonged passage of the gas the crystals gradually redissolved as thallous bicarbonate. A small sparingly soluble residue, obviously consisting of carbonates of other metals, was rejected. On adding fresh thallous hydroxide solution to the concentrated solution of the bicarbonate, a fine crystalline precipitate of thallous carbonate again separated. Purification was effected by evaporating a concentrated filtered solution of the bicarbonate to small bulk. Carbon dioxide was freely evolved during the evaporation, and the thallous carbonate was finally obtained in almost colourless crystals. The salt was then dried by exposure over soda lime in a desiccator.

The following observations on the stability and non-hygroscopic character of the compound are relevant to its use in analytical work. Thallous carbonate (8·4902 g.) was exposed in an open weighing tube to the atmosphere of the laboratory for 24 hours. The weight was then 8·4907 g. The salt was transferred to a desiccator containing soda lime and left for two days, after which its weight was 8·4905 g. It was then heated at 100° C. for two hours and cooled in the desiccator for three hours; the final weight was 8·4900 g. The extreme change of weight under these varied conditions was therefore less than one part in ten thousand.

Qualitative and quantitative comparison with extremely pure sodium carbonate as regards the behaviour with different indicators showed that the preparations were free from bicarbonate, and therefore suitable for preparing accurate standard solutions.

Standardisation of Acids.—As an example, the use of thallous carbonate for standardising nitric acid may be cited. Fifty ml. of a solution of thallous carbonate, containing 23·207 g. of Tl_2CO_3 per litre, required 43·2 ml. of nitric acid, the end-point being determined with methyl orange screened with xylene cyanol FF, as recommended by Hickman and Linstead (*J. Chem. Soc.*, 1922, **121**, 2502). The *p*H at the end-point was 3·8. The concentration of nitric acid was therefore 7·22 g. per litre.

By way of comparison a determination was carried out with AnalaR potassium bicarbonate under identical conditions. Fifty ml. of potassium bicarbonate solution (9·779 g. of $KHCO_3$ per litre) required 42·7 ml of nitric acid. The concentration of nitric acid was thus 7·21 g. per litre.

Standardisation of Potassium Iodate.—I have previously shown (ANALYST, 1926, **51**, 137) that thallous salts can be oxidised quantitatively by potassium iodate in presence of a high concentration of hydrochloric acid. The reaction with thallous carbonate takes place as follows:

$$Tl_2CO_3 + KIO_3 + 8HCl = 2TlCl_3 + KCl + ICl + 4H_2O + CO_2.$$

Ten ml. of a solution of thallous carbonate (23·207 g. of Tl_2CO_3 per litre) required 30·2 ml. of a solution of potassium iodate, the end-point being determined with the aid of chloroform. The concentration of potassium iodate was therefore 3·516 g. per litre.

This result was checked by titrating AnalaR potassium iodide under identical conditions. Fifty ml. of potassium iodide (5·223 g. of KI per litre) required 47·9 ml. of potassium iodate solution. The concentration of potassium iodate, as thus determined, was 3·516 g. per litre.

It will be evident that thallous carbonate has much to recommend it as a standard substance. The equivalent weight is unusually high—234 as an alkali and 117 as a reducing agent in an Andrews titration—and, as has been mentioned, the compound is easily prepared in a high degree of purity. At the same time no substance will command general satisfaction as a standard until it has received prolonged experimental study in the hands of a large number of independent workers. It is therefore much to be desired that chemists should subject the compound to the most careful scrutiny.

A. J. BERRY

THE UNIVERSITY CHEMICAL LABORATORY
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THE EXCRETION OF BISMUTH AND ITS ESTIMATION IN URINE AND FAECES

A FEMALE patient, 57 years of age, was admitted to hospital suffering from severe polyneuritis, and died 19 weeks later from hypostatic pneumonia resulting from the polyneuritis. Both lead and bismuth were detected in the urine, the amounts present being determined 31, 43, and 59 days after the patient's admission. The lead and bismuth were extracted and separated by combining the Allport and Skrimshire method (ANALYST, 1932, **57**, 440), and the S.P.A. method for determining lead (ANALYST, 1935, **60**, 541). Each was estimated colorimetrically, as sulphide, in alkaline solution. The bismuth was identified by the tests used by Lynch, Slater and Osler (ANALYST, 1934, **59**, 787). Alternatively, the S.P.A. method, only, was used.

The following results were obtained with samples of the urine:

Days after admission	Lead mg. per litre	Bismuth mg. per litre
31	0·09	1·09
43	0·25, 0·25	2·00, 2·00
59	0·05, 0·05, 0·06	1·52, 1·48, 1·60

A specimen of faeces, taken 60 days after admission, contained 6·0 mg. of bismuth and 2·3 mg. of lead per 100 g. of dried material.

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USE OF THE LOVIBOND TINTOMETER FOR THE COLORIMETRIC ESTIMATION OF FORMALDEHYDE BY THE PHLOROGLUCINOL METHOD

COLLINS and Hanzlik (*J. Biol. Chem.*, 1916, **25**, 231; Abst., ANALYST, 1916, **41**, 283; Hanzlik, *J. Biol. Chem.*, 1920, **42**, 411) based a method of estimating formaldehyde in dilute aqueous solution on its colour reaction with a phloroglucinol reagent, the colour being compared after 3 minutes with the colours of mixtures of Congo red and methyl orange. Spoto (*Diagnostica Tec. Lab.* (*Napoli*) *Riv. mensile*, 1931, **2**, 362) found that mixtures of alizarin yellow R with methyl orange made better colour standards; he allowed 5 minutes for the colour to develop.

In experiments on the influence of volume and temperature of the reagent, we have found that with a volume of 0·6 ml. for concentrations of formaldehyde between 1·6 and 32 p.p.m., and of 0·9 ml. for concentrations between 32 and 65 p.p.m., an error of 5 per cent. in measuring will only slightly affect the maximum colour. Variations of temperature between 15° and 30° C. have no effect upon the maximum colour, but a large influence on the rate of development and fading.

METHOD.—The experimental conditions for accurate estimation are embodied in the following outline of the method:—Measure 25 ml. of the formaldehyde solution (at 15° to 30° C.) into a 50-ml. measuring cylinder previously washed out with some of the solution. Add the phloroglucinol reagent (1 g. in 100 ml. of 10 per cent. sodium hydroxide solution) in the proportion of 0·6 ml. for concentrations of formaldehyde between 1·6 and 32 p.p.m. or 0·9 ml. for 32 to 65 p.p.m. After stirring the mixture, use it to rinse and fill a tintometer cell of suitable thickness. Begin the observation of colour within two minutes from the time the reagent was added and continue until the maximum is passed, *i.e.* for about 4 minutes longer, depending on the temperature. The tintometer is always set with 1·0 unit of brightness (neutral tint). Calculate the concentration of the formaldehyde solution from the maximum colour (red units) developed, by means of the following equation:

$$R = 0{\cdot}414tC + 1{\cdot}2$$

$$\text{or } C = \frac{R - 1{\cdot}2}{0{\cdot}414t}$$

where R represents the colour in Lovibond red units, *t* the thickness of the cell in inches, and C the concentration of formaldehyde in parts per million.

In test experiments with solutions containing from 1·6 to 65 p.p.m. of formaldehyde the red units observed agreed with the calculated values within ±0·1 to 0·2 unit (+0·4 with 1·6 p.p.m.).

The colour produced in the reaction is almost a pure orange, but it was found that the red could be observed much more accurately than the yellow. For this reason only red units are used in the equations and yellow units are disregarded. It was found that 1·0 unit of brightness (neutral tint) was generally required.

We wish to express our thanks to the Directors of the British Xylonite Company, Ltd., for permission to publish this note.

R. C. HOATHER
P. G. T. HAND

LABORATORY, LACTOID WORKS
THE BRITISH XYLONITE CO., LTD.
HALE END, LONDON, E.4

September, 1938

Official Appointments

THE Minister of Health has approved the following appointments:

HUGH CHILDS as a Public Analyst for the County of Nottingham, in addition to John Evans (November 15, 1938).

HUGH CHILDS as a Public Analyst for the County Borough of Rotherham, in addition to John Evans (November 16, 1938).

HUGH CHILDS as a Public Analyst for the County Borough of Doncaster, in addition to John Evans (November 21st, 1938).

HUGH CHILDS as a Public Analyst for the County Borough of Sheffield, in addition to John Evans (November 23rd, 1938).

The Ministry of Agriculture and Fisheries has approved the following appointments since May 20th, 1938:

E. R. ANDREWS as Agricultural Analyst for the County of London, vice E. T. Shelbourne.

C. J. REGAN as Deputy Agricultural Analyst for the County of London.

H. CHILDS as Deputy Agricultural Analyst for the County of Nottingham and, for the six months ending April 29th, 1939, for the County Borough of Sheffield.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

LONDON COUNTY COUNCIL

ANNUAL REPORT OF THE CHEMICAL BRANCH FOR 1937

THE Report* of the County Medical Officer of Health includes a section on the work of the Chemical Branch. In addition to statistical information of analyses, mainly of materials bought by the Council for use in its numerous institutions or for its other activities, the Report gives details of a number of chemical investigations.

SCHOOL MEALS.—In connection with the provision of meals for necessitous children, 107 samples were examined during the year. Included in this total were samples taken from 51 complete two-course meals. The standard adopted is that each meal shall contain not less than 25 g. of protein and have a heat value of not less than 750 calories. The average of the samples examined was 28·6 g. of protein and 732 calories. Where the requirements were not fulfilled, suggestions were made as to the steps that should have been taken to avoid the deficiencies.

TOXICITY OF PRODUCTS FROM THE USE OF FIRE EXTINGUISHERS.—At the request of the chief officer of the London Fire Brigade, an investigation was carried out as to the relative toxicity of the products from the use of fire extinguishers of the carbon dioxide, carbon tetrachloride, and methyl bromide types. A "standard" fire was generated in a small room by ignition of wood wool and high tension cable. The fire was then extinguished by the use of one of the extinguishers and samples of the atmosphere in the room at different levels were collected at once, and after an interval, by aspiration through glass gas tubes. The contents of the tubes were analysed to determine the proportions of various toxic gases present, such as carbon monoxide, carbon dioxide, chlorine, bromine, hydrochloric acid, hydrobromic acid, carbonyl chloride and carbonyl bromide. Taking into consideration the results of the analyses and information gained from a research into the available scientific literature on the toxicity of these substances, it was concluded that methyl bromide and carbon tetrachloride under the conditions of test could produce acid vapours of such a concentration as would be dangerous in an enclosed space unless a mask were worn. Although carbonyl chloride (phosgene) and carbonyl bromide were not found in appreciable quantity, the possibility of their formation under special circumstances must be borne in mind. In order to extinguish a fire with carbon dioxide it appears that a concentration of this gas is required which must be regarded as a possible danger in a confined space unless a mask is worn; the time required to extinguish a fire by this means is also longer than when using methyl bromide. The final opinion expressed was that there is no more risk involved in the use of methyl bromide and carbon tetrachloride extinguishers than when carbon dioxide alone is used. With each it would be necessary to use a mask if the fire were in a confined space.

ACTION OF SULPHATES ON CONCRETE.—Much discussion has taken place in professional circles, and many papers have been published, on the question of the effect of sulphates, in water or subsoil, on Portland-cement concrete. The matter has been investigated during the year, and work is still being continued in connection with one of the Council's housing estates where the clay has been found to contain a small amount of sulphuric anhydride present as soluble sulphates, and also appreciable quantities of pyritic matter and selenite which may cause damage to Portland-cement concrete especially in the presence of water. A sample of water from this site was found to contain soluble sulphate considerably in excess of that found in normal surface water.

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* Public Health, No. 3380. 1938. To be obtained from P. S. King & Son, Ltd., 14, Great Smith Street, Westminster, S.W.1. Price 1s.; post free 1s. 2d.

THE ATMOSPHERE IN VEHICULAR TUNNELS.—The systematic investigations, begun in 1928, on the condition of the air in Blackwall and Rotherhithe tunnels, were continued during 1937; 101 and 104 samples of air, respectively, from these tunnels were examined for carbon monoxide content and 26 from each for black suspended matter. The increase in motor traffic using the tunnels has continued at the same considerable rate at which it has been occurring since this work was started. However, on the whole, the atmospheric conditions can be said to have been no worse than in the previous year. The chief engineer has in hand works that will effect a large increase in the ventilating capacity of the plant at Blackwall tunnel.

Ministry of Health

LEAD IN FOOD*

IN this Report, Dr. Monier-Williams collects and examines the information available on the subject, with a view to arriving at some conclusions as to the significance of traces of lead in food and suggesting the best methods for its determination.

ABSORPTION, EXCRETION AND STORAGE OF LEAD IN THE BODY.—Lead may be taken into the system from many sources—through the lungs from dust, through the skin from grease paints and cosmetics containing lead, and through the alimentary canal from food. From a consideration of the published results (quoted in detail) the conclusion is drawn that under certain conditions lead may be quickly eliminated from the intestinal tract. Much of this lead is probably excreted by the liver into the small intestine and eliminated in the faeces. Some of it reaches the systemic circulation, whence it is partly excreted in the urine and partly stored in a comparatively innocuous form in the skeleton.

A normal person may excrete daily 0·05 mg. in the urine and 0·3 to 0·4 mg. in the faeces. Normally, systemic blood contains about 0·2 p.p.m. of lead, and the amount rises to 0·6 to 0·7 p.p.m. in the blood of persons suffering from lead poisoning.

The bones of a normal person may contain from 50 to 100 p.p.m. of lead, equivalent to 0·75 to 1·5 g. in the whole skeleton. It seems probable that under certain conditions lead may be released from the store in the bones into the systemic circulation and give rise to symptoms of lead poisoning. The tissues of the body, other than the skeleton, do not retain lead in any considerable amount.

THE LEAD-CONTENT OF FOOD.—Results previously recorded are summarised with references to the original publications. Among the foods and food ingredients that have been found to contain excessive quantities of lead are tartaric and citric acids, acid calcium phosphate, food colours, cider, tea, curry powder, aerated waters and sardines. The amounts of lead in various foods were determined in the Foods Laboratory of the Ministry of Health, and the following table gives some of the principal results obtained with certain individual samples (one, except where otherwise mentioned). They are not to be taken as representative but only as a general indication. In view of Chapman's finding of 1·5 and 6·4 p.p.m. of lead in two samples of lobster flesh (ANALYST, 1926, 51, 564), it was unexpected not to find any in the flesh, although appreciable amounts were present in the shell.

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* Reports on Public Health and Medical Subjects. No. 88. By G. W. Monier-Williams, O.B.E., M.C., Ph.D., F.I.C. Pp. 51. 1938. H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 1s. net.

	Lead p.p.m.
Fruits	
Strawberries (stalks removed)	0·4
Cherries (stalks removed)	0·5
Gooseberries	0·3
Redcurrants (stalks removed)	0·2
Blackcurrants	nil
Black grapes (imported)	0·5
Peaches	0·9
Pears (imported)	0·4
Oranges (pulp)	0·5
Bananas (as eaten)	0·6
Apples (as purchased)	0·3
Vegetables	
Tomato purée (2)	nil
Tomato juice	nil
Canned peas (imported)	nil
Canned peas (home-grown)	0·8
Runner beans (fresh)	0·3
Green peas (fresh)	0·2
Dried peas	1·1
Milk foods	
Malted milk	0·4
Chocolate milk (2)	1·2
Condensed milk (unsweetened)	nil
Butter	nil
Wrapped cheese (2)	nil
Meat foods	
Beef paste	nil
[illegible] beef (canned)	nil
Beef bone (imported)	6·8
Chicken and ham paste	nil
Meat extract	1·6
Meat cubes (2)	2·0, 2·4
Condiments	
Black pepper	2·0
White pepper	1·0
Curry powder	1·8
Curry powder	21·6
Mustard	nil
Ground ginger	0·4
Ground cloves	4·0
Ground nutmeg	0·2
Sauces (2)	nil
Gravy (dried)	4·4
Canned and bottled fruits	
Pears (imported)	nil
Peaches (imported)	nil
Apricots	0·2
Pineapple	0·3
Dried and crystallised fruits	
Apple rings	0·2
Prunes	0·6
Raisins	nil
Figs	nil

	Lead p.p.m.
Cereals	
Cake mixture	0·5
Oatmeal	nil
Corn flakes	nil
White bread	0·2
Rice	0·4
Self-raising flour	2·4
Fish foods	
Salmon and shrimp paste	0·4
Sardine paste	8·3
Brisling (2)	0·3, 0·5
Shrimp (aluminium container)	0·3
Silds (aluminium container)	5·1
Silds (in tinned can)	0·3
Herring roes	0·4
Lobster flesh (2)	nil
Lobster shell	3·4
Crab	0·3
Oysters	0·2
Whelks	0·2
Whelks	2·1
Winkles	1·5
Beverages	
Lemonade crystals	nil
China tea (loose, as bought)	1·9
China tea (in lead foil)	4·4
China tea (in lead foil)	6·1
Indian tea (loose, as bought)	10·2
Ground coffee	0·4
Coffee essence	0·3
Stout	nil
Miscellaneous	
Turmeric root	282·5
Turmeric root	10·0
Liquid saffron (colour)	5·2
Apricot yellow (food colour)	44·0
Damson blue paste (food colour)	337·0
Apple green paste (food colour)	85·0
New-laid eggs	nil
Dried eggs	nil
Tap water (Westminster)	0·03
Baking powder (alum and phosphate)	7·1
Baking powder (tartrate)	1·1
Demerara sugar	0·6
Blackcurrant jam	nil
Plum jam	nil
Lard	nil
Margarine	0·3
Gelatin (powdered)	2·0
Custard powder	nil
Custard powder	1·2
Blanc mange powder	1·0

LIMITS FOR LEAD IN FOOD FROM THE PUBLIC HEALTH VIEW-POINT.—From a consideration of these figures and results previously recorded the following conclusions are drawn: It would appear that, normally, about 0·2 to 0·25 mg. of lead is likely to be ingested daily with food, but that if certain items of high lead-content are added to the diet, the total amount of lead ingested may become excessive. The total daily intake of lead from all sources, including water, is normally about 0·5 mg. An intake of 1 mg., or possibly even less, must be regarded with suspicion.

In discussing permissible limits for lead in various articles of food the important point is not whether the limits themselves are "safe," but what their effect would be on the total intake of lead.

In all probability there is a wide range between the limit for toxicity and a lower limit for safety below which the harmfulness of lead may be assumed to be negligible. This lower limit of safety is unknown and it is therefore desirable to reduce the lead in food to the lowest amount possible.

DETERMINATION OF LEAD IN FOOD.—The more important methods that have been used at various times for determining lead in foods and biological material are summarised and critically discussed under the following heads:—(i) Destruction of organic matter. (ii) Separation as sulphide. (iii) Precipitation as oxalate. (iv) Extraction and determination with dithizone. (v) Separation with sodium diethyl-dithiocarbamate. (vi) Separation by electrolysis. (vii) Precipitation as sulphate. (viii) Colorimetric determination as sulphide. (ix) Determination as chromate. (x) Nephelometric determination as sulphate. (xi) Special methods for calcium phosphate. (xii) Separation of iron and bismuth as thiocyanates. (xiii) Spectrographic methods. (xiv) Use of radio-active lead in physiological research. (xv) Nitrite test.

GENERAL METHOD.—The method used in obtaining the results in the foregoing table was practically the same as that of Allport and Skrimshire (ANALYST, 1932, **57**, 440), with the addition of lead sulphate precipitation as carried out by Francis, Harvey and Buchan (ANALYST, 1929, **54**, 725). The method of Allport and Skrimshire, without precipitation of lead sulphate, does not differentiate between lead and bismuth, and it is not always safe to assume that bismuth is absent from foods. A further advantage of lead sulphate precipitation is that it ensures that a perfectly colourless solution is obtained for the colorimetric determination.

For the determination of lead in samples that contain much calcium phosphate (*e.g.* bone or baking powder), a method similar to that of Roche Lynch, Slater and Osler (ANALYST, 1934, **59**, 787) was used.

By the combination of the methods described satisfactory results were obtained in presence of as much as 1000 p.p.m. of tin, iron or magnesium. With certain synthetic food colours, containing very large quantities of tin, and possibly other metals, it may be necessary to use the special method of the S.P.A. (ANALYST, 1935, **60**, 541) or that given by Allport and Skrimshire (*loc. cit.*).

The Report concludes with 11 pages of references to papers published (with a few exceptions) during the last 12 years. In each instance the subject matter of the paper is indicated.

Department of Scientific and Industrial Research

REPORT OF THE CHEMISTRY RESEARCH BOARD FOR THE TRIENNIAL PERIOD ENDED DECEMBER 31, 1937*

THE Report reviews the progress of the research undertaken at the Chemical Research Laboratory during the three years that have elapsed since the publication of the last Report (*cf.* ANALYST, 1935, **60**, 613), and includes the Report of the Director (Sir Gilbert Morgan). Much of the work described is of a long-term character, as for instance, the researches on the corrosion and tarnishing of metals, the study of coal and tar, and the investigation of the rarer elements found within the British Empire. Other investigations of more immediate industrial application have been carried out at the request of, and mainly at the expense of, the industries concerned. References are given to over 70 papers dealing with the work published in scientific and technical journals and to 16 patents covering results of various aspects of the work, including the fundamental patents on the use of synthetic resins in water purification.

CORROSION OF METALS.—A prolonged enquiry into the causes of corrosion and their prevention is in progress, and concurrently with this research, investigations of a technical character, such as the corrosion of locomotive boiler-tubes, have been carried out in co-operation with the London, Midland and Scottish Railway.

Corrosion of Locomotive Boiler Tubes.—Preliminary experiments showed that localised pitting was unlikely to be caused by impurities in the metal, nor could intercrystalline corrosion due to attack by alkalis at high pressures and temperatures be detected in corroded tubes. The corrosion products at boiler temperature consist largely of nearly black ferroso-ferric oxide which may be precipitated either in a loose sooty condition, or as a coherent varnish-like scale, or in intermediate forms. The particular form is influenced by the composition of the water and probably other factors. The tube thus becomes covered with a more or less continuous layer of oxide which overlies the very thin film of "mill-scale" formed in the last stages of tube manufacture, and the layer may contain calcium or magnesium salts, or both, precipitated from solution. Pits form where the conditions are locally unsuitable for the formation of this layer in a protective form. Corrosion is mainly of the oxygen absorption type, but small amounts of hydrogen are probably evolved, and the evolution centres may perhaps give rise to pits. The condition of the mill-scale determines to some extent the area over which general corrosion (roughening) occurs.

Protection of Magnesium Alloys by the Selenium Process.—Magnesium alloys are particularly susceptible to corrosion by chloride solutions, and their use for aircraft, etc., exposed to marine atmospheres or to sea-water is dependent on adequate protection by some form of corrosion-resisting film or layer. The best results were obtained by depositing a film of selenium produced by immersing the alloy for 5 to 10 minutes in a solution containing 10 to 15 per cent. of selenious acid and 0·5 per cent. of sodium chloride. Protective films have also been formed by rubbing the alloy with cotton-wool saturated with the solution. The protection afforded by the selenium film may be increased by over-coats of suitable paints.

Corrosion of Magnesium Alloys by Leaded Petrol Fuels.—The attack is probably caused by hydrolysis of the tetraethyl lead in the presence of ethylene dibromide and water to form lead bromide or ethylated lead bromides which deposit low overvoltage cathodes of metallic lead on the alloy. Of the large number of inhibitive substances examined, the best results were obtained by adding quinoline to the fuel. The addition of 1 per cent. suppressed corrosion in a test of six months' duration.

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2 1938. Price 3s. net.

Production of Green Patina on Copper.—Thionyl chloride, applied in the form of a spray, to copper roofs, especially those blackened by exposure, produces a coating which improves in appearance with subsequent exposure and yields a satisfactory patina after only a few months (B.Pat. Appl., No. 28541/37).

HIGH-PRESSURE RESEARCH.—The technique of high-pressure operations has been studied for several years at the Laboratory, and the Report gives details of experiments on the synthesis of acetic acid from methyl alcohol and carbon monoxide, and of studies in the production of higher aliphatic acids.

Acetic Acid Synthesis.—Further experiments have confirmed the previously reported yield of approximately 80 per cent. It would appear to be impracticable to make acetic acid from water-gas without isolating methyl alcohol as an intermediate product.

COAL, TAR AND RUBBER RESEARCHES.—A research on the constitution of coal has been initiated recently, and an extended study of coal tars, especially of those derived from low-temperature carbonisation, has been in progress for several years and has resulted in a valuable extension of knowledge of tar constituents. Catechol, a product for which this country is now dependent on imports and which is used as a starting point in the preparation of several important drugs and fine chemicals, has been found in low-temperature tar. Technical methods have been devised which should lead to the industrial production of this compound from liquors that have hitherto been a waste product. Attention has also been directed to tars to improve their value as road materials.

The possibility of compounding rubber and tar with a view to establishing its use on the roads and for other industrial purposes is also being investigated in co-operation with the rubber-growing industry.

Tar Stills.—The introduction of vertical retorts for the carbonisation of coal has led to the production of tars which are considerably more corrosive to tar stills than tars derived from horizontal retorts. Since the introduction of vertical retort tar, the life of certain stills has diminished from 16,000 to 30,000 tons to an average of 7000 to 8000 tons when dealing with tars composed approximately of 75 per cent. of vertical and 25 per cent. of horizontal retort material. It was calculated that this reduction in the life of a still by 50 per cent. was equivalent to 5d. per ton of tar distilled and that the total cost to the tar distillation industry was of the order of £25,000 annually. A detailed inquiry into the causes of corrosion of stills has been made at the request of the industry and has resulted in suggestions for reducing the activity of the corrosive elements.

Chlorinated Rubber.—The different types of products that can be made with chlorinated rubber have received attention. Sheets of linen were impregnated with a solution of chlorinated rubber in benzene or carbon tetrachloride and the solvent was removed when the sheets were submitted to pressure at 140° C. If the materials were allowed to cool under pressure, hard, dense boards were obtained, but if the pressure was released when the ingredients were hot, very light laminated materials of a cell-like structure resulted. Chlorinated rubber can be used with various fillers, such as asbestos, woodmeal, etc., as a moulding material giving products of considerable strength. The most striking of its properties is that it can be utilised as a plastic without the addition of any filler. When compacted under pressure of one ton per square inch at 115° C. to 120° C. for a short period, an opaque moulding is produced when the pressure is released at this temperature. If, however, the pressure is retained while the mould is cooled to about 70° C., a completely transparent moulding is obtained. Transparent films of chlorinated rubber are readily obtained by slow evaporation of benzene or carbon tetrachloride solutions. Chlorinated rubber unites with basic colouring matters in a remarkable manner. When the carbinol base of rosaniline or of brilliant green is dissolved in the benzene solution of chlorinated rubber, the colour of the dye is rapidly developed. On evaporation of the solvent, coloured films remain from which the dye is not readily extracted by water, dilute acids or alkalis. Such coloured material could be utilised in the production of transparent moulded articles.

SYNTHETIC RESINS.—Investigations, such as that on the structure of phenolic resins, have been continued in conjunction with efforts to develop more immediate applications of resinous materials, notably those resins that possess base-exchange and acid-exchange properties. The remarkable properties of these substances were discovered at the Teddington laboratory (*cf.* ANALYST, 1935, **60**, 614; 1936, **61**, 33; 1937, **62**, 302). In the present Report an account is given of the pyrolysis and structure of phenolic resins, their X-ray examination, and their electrical properties. The use of natural phenolic substances, such as catechin and gambier, as a cheap component in the manufacture of resins in place of phenols derived from tar, has received attention. These resins can be used in the industrial preparation of laminated boards. Investigations have also been made on ketone resins of the transparent, glass-like variety which are becoming of increasing interest, notably in the motor-car and aircraft industries.

CHEMOTHERAPY.—An investigation of new bases of the pyridine series that may be of service in chemotherapy is in progress. A new series of heterocyclic derivatives has been discovered, to which the generic name of 1:3-diazalines has been given.

Neocryl.—A new drug, succinanilomethylamide *p*-arsonic acid, now known as "neocryl," has been discovered and is being clinically tested by the Therapeutic Trials Committee of the Medical Research Council, for the treatment of syphilis and African sleeping sickness. Present indications are that it is less toxic than drugs already in use.

RARE METALS.—Successful attempts have been made to extract some of the rarer metals known to exist in coal or coal ash and also found in the flue dusts which accumulate in the producer gas mains and waste gas flues of gas works. Gallium, germanium, indium, cerium, thallium, lanthanum and silver were all recognised and recovered, in varying but mostly very small amounts, and further attention will be directed to the utilisation of certain of these metals, for example, gallium and germanium.

In these investigations a quantity of Australian molybdenite was treated for the rhenium it contained, and use was made of the di- and tri-pyridyls obtained by the dehydrogenation of pyridine. Dipyridyl has proved to be a valuable reagent for the study of the constitution of complex metallic salts, and specimens of the base have been supplied to other British laboratories for this purpose. Furthermore, dipyridyl, when combined with salts of ruthenium, gives rise to an exceptionally stable orange red trisdipyridyl ruthenous chloride which has been resolved into its optically active components. Tripyridyl, which has hitherto been prepared exclusively in the Laboratory, may be used as a very delicate reagent for ferrous iron in sea water (at a dilution of one part in two million parts of water), and a specimen was employed in this way in a recent expedition to the Indian Ocean.

Recently two higher polypyridyls, tetrapyridyl and a hexapyridyl, have been isolated; these new bases develop characteristic colours with metallic salts.

MICROBIOLOGY.—Bacterial investigations were called for in dealing with problems as diverse as the preservation of ropes and cordage against decay, the discoloration of paintwork, the origin of an unpleasant bacterial odour in beer, the corrosion of water mains and petrol storage tanks, and the cause of an earthy flavour in salmon. In all these problems bacteria have played a destructive part, but acetic acid bacteria, especially *B. suboxydans*, are utilised constructively in the preparation of sorbose, an essential step in the production of synthetic vitamin C from glucose. One common disadvantage attending the employment of bacteria is the excessive time they sometimes take in effecting their transformations. With the acetic acid bacteria, however, it has been shown that the period can be reduced substantially by blowing fine bubbles of air through the fermentation liquid. In this way the time required for one stage of the process has been reduced from 12–15 days to less than 2 days.

Investigations on the biochemistry of the lower fungi are now being conducted under the direction of Professor Raistrick. Earlier work on the subject has shown that many new organic compounds can be made economically from sugar by the use of different species of fungi, and, although these new products of mould metabolism are at present of purely academic interest, future work may well lead to developments of industrial importance.

New Zealand

Department of Agriculture

ANNUAL REPORT OF THE CHEMISTRY SECTION FOR 1937–1938

THE activities of the Chemistry Section, under the direction of Mr. R. E. R. Grimmett, M.Sc., are closely co-ordinated with those of other Divisions of the Department and of the Department of Scientific and Industrial Research, and a certain measure of amalgamation with the Dominion Laboratory has been brought about. In addition to investigation related to advisory work, a number of special problems have been studied.

DEFICIENCY DISEASES OF LIVESTOCK.—*Bush Sickness.*—The demonstration of the importance of cobalt to livestock has been followed by developments in other directions through the co-ordinating activity of the Cobalt Committee. The Chemistry Section is undertaking work in the North Island and the Cawthron Institute in the South Island. A comprehensive series of soil and pasture samples has been collected, and McNaught's successful application of the "R-salt" method (*cf.* ANALYST, 1939, p. 23) has provided valuable confirmation of field evidence. Under conditions of spring growth, with ordinary but not extreme precautions to avoid soil contamination, it has been found that pastures that are bush sick for both cattle and sheep contain from 0·01 to 0·04 p.p.m. of cobalt, those sick for sheep but not for cattle from 0·04 to 0·07 p.p.m., and healthy pastures from 0·07 to 0·3 p.p.m. or more. Pastures from specially enclosed plots on extremely bush-sick country, as at Kopaki, may contain less than 0·01 p.p.m. of cobalt. In experiments with cobalt top dressing, in which 1/4 to 2 lb. of cobalt sulphate was used in admixture with superphosphate or cobaltised superphosphate, very definite results in improved health and increased weight of sheep and lambs have been obtained, and analyses indicate that the cobalt-content of the pastures may be increased after several weeks of top dressing by as much as tenfold, and that amounts above the critical value for stock health are still maintained six months later. Bush-sick pastures show a slight rise, and healthy pastures a much greater rise in cobalt-content in late summer.

Phosphorus Deficiency in Cases of Osteomalacia.—In several cases of pica, osteomalacia, etc., it was suspected that the disease was associated with deficiency of phosphorus or an unbalanced ratio of phosphorus to calcium. On a property at Onewhero, near Tuakau, Raglan County, very persistent bone and stick chewing had occurred among dairy cows, and over a number of years young cattle and sheep failed to thrive. Analyses at the Veterinary Laboratory had demonstrated low levels for inorganic phosphorus in the blood. Samples of soil and pasture, when analysed, supported the contention that deficiency of phosphorus was the cause of the trouble. The soils were leached volcanic ash loams with high lime requirements, high soluble alumina probably resulting in strong phosphate fixation, and with very low contents of total and available phosphoric acid. The pastures contained approximately 1 per cent. of calcium oxide, but only about 0·4 per cent. of phosphoric acid. It was subsequently demonstrated that feeding with bone-meal, when persisted in long enough, would overcome the stock trouble.

In connection with an outbreak of bandiness in hoggets near Balclutha, turnips on which the animals were being fed were submitted for analysis. The roots from Balclutha contained 0·43 per cent. of calcium oxide and 0·75 per cent. of phosphoric acid on the dry weight, whilst other turnip roots from Ruakura for comparison contained from 0·6 per cent. to 0·7 per cent. of calcium oxide and 0·4 per cent. of phosphoric acid.

MINERAL DEFICIENCIES AND FRUIT TREE GROWTH.—A considerable number of citrus-tree leaves have been analysed in connection with a chlorotic condition of the leaves and general unhealthiness of the trees. Some indications of positive response to zinc spraying have been obtained by the Horticulture Division in the Tauranga area, and analyses point to a zinc-content of the young leaves of from 5 mg. to 20 mg. per kilo. of dry matter being associated with such conditions, while healthy trees usually have a higher zinc-content.

In the Auckland district joint investigations by the Horticulture Division and the Department of Scientific and Industrial Research indicate a deficiency of manganese as a contributing factor to chlorotic conditions, and leaves of the affected trees were found to vary in zinc-content from 16 mg. to 31 mg. per kilo., and in manganese-content from 5 mg. to 12 mg. per kilo.

Samples of leaves taken under a standard system have been obtained from manurial trials in apple orchards. The analytical results will be compared with those indicated from qualitative and quantitative observations on the yield and vigour of the trees.

TOXICITY OF ZINC TO PIGS.—Two further experiments in which pigs were fed with pure zinc lactate showed that an intake of 0·05 to 0·005 per cent. in the milk fed were associated with death and with a non-specific arthritis. High amounts of zinc have been found in the organs. The total amount of zinc required to cause death has been as low as 37 g. given over two months. Several cases of suspected poisoning of pigs from milk passed through galvanised-iron pipe lines have again occurred, and analyses have confirmed the presence of excessive zinc in the milk and in the organs of the pigs.

POISONING DUE TO ARSENIC SULPHIDE IN THE SOIL.—A case requiring intensive investigation occurred in the Reporoa district. This isolated farming community lies to the south of the Waiotapu thermal area and also has a number of thermal and mineral springs scattered over it. Dairying, dry stock, and sheep farming are all carried on, but results, both in stock health and production, have never been as good as might have been anticipated. Continued unthriftiness and mortality of dairy stock on one farm led to an analysis being made of mud and water from a drain; arsenic was found in both. Further investigation revealed that the mud deposited by the Waiotapu River was arsenical and that the swamp soils formed from this mud contained arsenic. The arsenic appears to be present both in combination with iron and as sulphide. Orpiment occurs in massive form in the sinters around some springs, and as a finely divided precipitate in pools receiving the overflow from the Champagne Pool at Waiotapu, the waters of which contain arsenic in solution. A large number of samples have been collected, and a survey of the whole settlement is in progress. Among samples so far analysed up to 3·75 mg. of As_2O_3 per 100 ml. have been found in some drainage waters, 2·5 per cent. in muds, 0·3 per cent. in soils, 2·3 mg. per 100 g. in dry matter of grass, and 0·6 mg. and 0·25 mg. per 100 g., respectively, in the dry marrow and femur bone of a cow that had died under suspicious circumstances.

CHEMICAL CONTROL OF RAGWORT.—The Agricultural Chemist (Mr. F. B. Thompson) has investigated the conditions for the most successful use of sodium chlorate. Chlorate injury could be traced by the red colour imparted to the affected roots of the plants. All the experiments indicated that the ragwort plant has great difficulty in absorbing and translocating within its tissues sufficient sodium chlorate to kill the whole length of the roots, but that very little chlorate will completely defoliate it. To kill the plant completely the doses had to be considerably larger than was first anticipated. Analyses of treated soil showed that the chlorate tends to remain on the top few inches. Atlacide, a proprietary sodium chlorate weedkiller, behaved in the same way as the pure salt. Comparative tests with other weed-killers, *e.g.* the sulphates and nitrates of copper and zinc, showed that approximately 15 g. of these compounds were required to produce an effect similar to that obtained with 1 g. of sodium chlorate. Dichromates, thiocyanates and bisulphites were also less effective than sodium chlorate. Much of the re-growth that has been attributed to fresh seeding is undoubtedly the result of incomplete killing of the roots.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

UNDER the Food and Drugs Ordinance various authorities are permitted to submit samples for analysis. According to the Government Analyst (Mr. Kenneth Wallis) 5129 samples were submitted, mainly by the Police Department, the Government Public Health Departments, the Mayors and Town Councils of Georgetown and Berbice, and the Superintendent of the Alms House. Of the 4238 samples of milk examined, 325 were adulterated. Special raids are unexpectedly made by the Police Department and Public Health Departments on Sundays, Public Holidays and after official hours. Of 983 samples thus taken, 120 were adulterated, the percentage rate being 12·2 as compared with 6·0 on ordinary week-days.

CRIMINAL INVESTIGATION.—Three hundred and forty-seven exhibits were examined, including 10 in cases of arson, 91 in 23 cases of alleged poisoning, and 150 in 23 cases of counterfeiting coins and notes.

Poisoning Cases.—The chief poisons found were arsenic, datura, sulphuric acid, mercuric chloride, belladonna liniment and ground glass.

Counterfeit Coins and Currency Notes.—The 150 exhibits examined included various coins, currency notes, moulds and crucibles. The moulds were made of plaster of Paris, and several showed excellent impressions of two and one shilling pieces. In some, flaws were found and photographed (enlarged), which corresponded with flaws in silver pieces previously examined. The composition of the fused masses in the crucibles agreed in most instances with that of the counterfeit coins. Several pieces of metal were also analysed in connection with these cases to ascertain if they could be used in counterfeiting.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

THE Government Analyst (Mr. G. W. Baker) reports that 12,330 samples have been examined, as compared with 9188 in 1936; the increase was mainly due to more intensive sampling made possible by the appointment of additional inspectors.

FOOD AND DRUGS.—Of the 7465 samples examined, 3985 were of milk (290 adulterated) and 2120 of semni (140 adulterated). Very large quantities of fat similar in appearance and flavour to, but containing no butter-fat, are imported from Europe. This fat is labelled in accordance with the provisions of the Ordinance, but there is no doubt that much of it is used as a substitute for, or adulterant of, semni.

Standard for Cream.—Under the Foods Ordinance a minimum of 35 per cent. of fat is required for cream, but this is now being reconsidered as the result of representations that the manufacture of tinned cream with so high a percentage of fat is impracticable.

Standards for Honey.—During the year standards for honey have been added to the regulations under the Foods Ordinance. They are as follows: "Honey means the nectar and saccharine exudation of plants gathered, modified and stored in comb by honey bees, without the addition of any colouring, flavouring, or other substance. Honey shall be laevorotatory and shall contain not more than 25 per cent. of water, not more than 0·25 per cent. of ash, and not more than 8 per cent. of sucrose."

Of the 30 samples of honey examined, 14 were adulterated.

Hypersensitivity to Iodine.—Among the 2260 biochemical specimens examined were the blood and urine of a patient who was hypersensitive to iodine. The blood contained 1·27 mg. per 100 g. and the urine 5·8 mg. per 100 ml.

POLICE DEPARTMENT.—*Poisoning Cases.*—In connection with 9 cases of suspected human poisoning, 33 specimens were examined. In five cases poison was found: arsenic in 2, mercury in 1, veronal in 1, and carbon monoxide in 1.

Shooting and Bombing.—Seventy-nine exhibits were examined. Most bullets and cartridge cases are now examined in the C.I.D., and it is only when a second opinion or chemical analysis is required that they are submitted to the Government Analyst.

Finger-prints on a Time Fuse.—The finger-prints on a time fuse were photographed with the aid of the specially constructed "cold stage" described in the 1936 Report (*cf.* ANALYST, 1938, **63**, 115). They corresponded with those of an arrested suspect.

Spreading of Ink as Evidence of Forgery.—In a case in which a will had been forged evidence of later additions was provided by the spreading of the ink into the creases of the paper in the added portions, and absence of such spreading in the rest of the document.

"ACTIVE ALUMINIUM" IN THE SOIL.—In an investigation to determine the relation of exchangeable cations to "active aluminium" in the soil it was found that there is a close relation between the valence of an adsorbed cation and the amount of "active" aluminium present. Potassium and sodium tend to decrease, whilst lithium and magnesium salts increase the aluminium toxicity of the soil.

Georgia Experiment Station

FIFTIETH ANNUAL REPORT, 1937–1938

THE Georgia Experiment Station was founded in 1887 by Act of the United States Congress, and is under the control of the University System of Georgia. During its 50 years of service the Station has issued 50 annual reports, 199 bulletins and 115 circulars, and has made many discoveries of benefit to agriculture.

RAPID CHEMICAL SOIL TESTS.—More than ten thousand rapid chemical tests have been made on 1200 soil samples taken from fields of known fertiliser treatment and crop response, and correlation studies between the laboratory data and response to fertilisation are in progress. In addition to showing the approximate amount of available nitrogen, phosphorus and potassium necessary to produce good crops on Georgia soils, the quick tests have indicated soil abnormalities other than deficiencies in any of these three elements. There are indications that aluminium toxicity is prevalent in parts of the State. The following data, obtained by rapid soil tests on two soils of widely different nature and location, suggest aluminium toxicity. The results are expressed in pounds per acre.

	Crop	Condition	*p*H	NO_3	P	K	Al	NH_3	Fe	Ca
Soil 1*a* ..	Corn	Fair	4·65	0	15	426	100	75	20	200
,, 1*b* ..	Corn	Dying	3·95	0	10	336	500	125	200	200
Soil 2*a* ..	Wheat	Fair	5·30	10	40	205	100	75	5	150
,, 2*b* ..	Wheat	Poor	4·55	15	15	111	500	50	5	100

COLCHICINE TREATMENT OF SEEDS.—This method holds interesting possibilities for the production of new varieties of pasture and forage plants. Seeds of the more important pasture and forage plants have been treated for varying periods of time, and approximate effective time-concentrations for some plants have been determined. Even rather light treatment of the seeds of some species so weakened and retarded the growth of the seedlings that an unusually high proportion died. It was surmised that the colchicine treatment may destroy or inhibit the production of the plant hormones needed for root and shoot development, and that treatment with Hormodin (or individual plant hormones) might overcome the retarding effect. Some of the legumes, but none of the grasses, responded definitely to hormone treatment. Alfalfa seedlings were much more vigorous when treated with Hormodin. This favourable reaction was used later for getting a greater survival of seeds of the creeping-rooted alfalfa, seeds of which were obtainable in only a limited quantity. Subterranean clover also reacted favourably to the Hormodin treatment subsequent to the colchicine treatment.

MANGANESE REQUIREMENTS OF COTTON.—Large well-fruited cotton plants have been grown repeatedly in nutrient solutions containing 0·1 p.p.m. of added manganese. It was found that cotton seedlings grown in a medium without added manganese developed deficiency symptoms in about three weeks. Under certain conditions a medium containing 0·01 p.p.m. of manganese produced almost as much vegetative growth as those containing larger amounts of the element.

PEACH STORAGE STUDIES.—Peaches stored at 33° to 36° F. in an atmosphere containing 10 per cent. of carbon dioxide were better preserved than in any other combinations of gases tried. Even at this concentration, however, the fruit had an undesirable flavour at the end of several weeks.

TOXICITY OF PEANUT MEAL FOR SWINE.—Swine fed for several days with large quantities of peanut meal developed toxic symptoms and some of them died. Preliminary investigation of this problem indicates that the effects are due, at least in part, to the comparatively high potential benzoic acid content of peanut meal. Although the amount of benzoic acid found in the urine of pigs fed on this material was considerably less than has been reported for cattle fed on the meal, it appeared to be high enough to cause a severe drain on the glycine supply of the animals.

New International Standard for Vitamin B_1

THE Medical Research Council has requested us to publish the following statement:

It is announced that the first International Standard for Vitamin B_1, which consisted of an adsorbate of the antineuritic vitamin, made from rice polishings, on fullers earth, has now been replaced by a preparation of crystalline Vitamin B_1 hydrochloride. In recent years progress in the study of the antineuritic vitamin has been rapid, and this change in the form of the International Standard has been made possible by the synthetic preparation of the vitamin in pure crystalline form.

Through the generosity of four manufacturers, an adequate quantity of the new crystalline material was placed at the disposal of the National Institute for Medical Research, Hampstead, to enable a new standard to be prepared consisting of the pure crystalline substance. Extensive international investigations of the properties of this material, and, in particular, the determination of its potency in terms of the original international standard by a variety of methods have now been completed, and the members of the International Conference on Vitamin Standardisation have unanimously recommended that the sample be adopted as the Second International Standard for Vitamin B_1, and that the International Unit be defined as the antineuritic activity of 3 microgrammes of the international standard preparation. This recommendation has been adopted by the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations.

As in the case of the other International Vitamin Standards, the new standard for Vitamin B_1 is held, on behalf of the Health Organisation of the League of Nations, at the National Institute for Medical Research, Hampstead, N.W.3, and is distributed therefrom to national control centres established in other countries for local distribution to laboratories, institutes and research workers; and to workers resident in countries in which the establishment of national control centres has not yet been completed.

With regard to the supply of the new standard for Vitamin B_1 to those requiring it in the United Kingdom, samples have already been sent to the laboratories, institutes and research workers who have hitherto received the standard adsorption product. Others requiring the standard are asked to make application to the Department of Biological Standards, the National Institute for Medical Research, Hampstead, N.W.3.

18th November, 1938

National Physical Laboratory

FEES FOR TESTS ON VOLUMETRIC GLASSWARE

THE Director of the Laboratory (Sir Frank E. Smith) has requested us to call attention to the issue of a new schedule of fees for tests on volumetric glassware, which came into operation on December 1st, 1938.

The new fees are on a nett basis and, generally speaking, are equal to less than the old fees, less the 33⅓ per cent. discount previously only obtainable on batches of one dozen or more vessels of the same type and capacity sent together for test.

The new schedule covers a considerably larger range of apparatus than the old schedule. Thus it now includes volumetric glass ware for testing milk and milk products.

British Standards Institution

THE following Standard Specifications have been issued*:

No. 647—1938. BRITISH STANDARD METHODS FOR TESTING GLUES. (BONE, SKIN AND FISH GLUES.)

This Specification, first published in December, 1935, and revised in September, 1938, is in two parts.

Part I.—General.—(1) Preparation of Sample. (2) Concentrations. (3) Testing of Liquid and Jelly Glues.

Part II—Methods of Test.—(A) Method for the Determination of Moisture-Content. (B) Determination of Jelly Strength. (C) Determination of Jelly Strength, using the Bloom Gelometer. (D) Viscosity. (E) Melting-point. (F) Foam. (G) Water Absorption. (H) Keeping Quality. (I) Joint Strength in Shear. (J) Reaction (*p*H). (K) Grease. (L) Ash. (M) Chloride. (N) Sulphur dioxide.

Diagrams are given of a test piece, a clamping device for retaining a joint under pressure, and the Bloom gelometer, and there is an appendix with notes on the use of apparatus described. These are not to be taken as excluding other manufacturers of chemicals or apparatus.

No. 809—1938. BRITISH STANDARD METHODS FOR THE SAMPLING OF DAIRY PRODUCTS.*

These Methods of Sampling form part of a series of British Standards for Use in the Dairying Industry, the preparation of which was authorised by the Chemical Divisional Council in 1933.

The methods include the sampling of milk, cream, butter, condensed milk, cheese, and milk powder, and include sampling both for chemical analysis and for bacteriological examination.

The standard also includes a description of various types of apparatus that have been found suitable for obtaining samples of various dairy products.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Chemical Evaluation of Spoilage in Canned Fish. F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 688–695.)—The traces of volatile fatty acids normally present in fresh canned fish consist mainly of formic and acetic acids. As decomposition proceeds there is a progressive increase in the volatile acid content and formation, in increasing amounts, of higher members of the series. The identity of all the higher members formed has not been established, but in tuna fish the highest member is normal butyric acid, and in salmon iso-butyric acid. The method consists in the determination of the "volatile acid number" and the "formic acid number." The finely minced fish (50 g.) is suspended in 100 ml. of water and treated with 15 ml. of 2 *N* sulphuric acid and 15 ml. of 20 per cent. phosphotungstic acid solution (with tuna fish 25 ml. of each reagent are used). The mixture is diluted to 250 ml., shaken, allowed to stand for 5 minutes, and filtered. The filtrate (150 ml.) is distilled at the rate of about 200 ml. per hour in Dyer's apparatus (*J. Biol. Chem.*, 1917, **28**, 445; Abst., ANALYST, 1917, **42**, 149), as modified by Clark and Hillig (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 684) after the addition of 0·5 ml. of 50 per cent. sulphuric acid (1 ml. for tuna fish) until two 100-ml. portions have been collected. Each portion is titrated with 0·01 *N* barium hydroxide solution, phenolphthalein being used as indicator, until the colour matches that of a buffer solution of *p*H 8·6 containing the same amount of indicator. After deduction of the result of a blank titration, the total number of ml. of 0·01 *N* acid corresponding with 100 g. of fish is termed the "volatile acid number." The two titrated liquids are combined and, after the addition of two drops of saturated barium hydroxide solution, evaporated to dryness. The residue is treated with 5 ml. of water and 1 ml. of *N* hydrochloric acid in excess of the amount necessary to liberate the volatile acids, and the solution is filtered. The combined filtrate and washings, the volume of which must not exceed 30 ml., are treated with 5 ml. of 10 per cent. aqueous sodium acetate solution, 5 ml. of 5 per cent. sodium chloride solution and 10 ml. of 5 per cent. mercuric chloride solution, and the mixture is heated beneath a reflux condenser on the steam-bath for two-and-a-half hours. The precipitate of mercurous chloride is weighed in a tared Pregl filter-tube counterpoised by a similar tube prepared and treated in the same manner. The weight of the precipitate ×0·0975 gives the weight of formic acid in the sample, and 3⅓ times this figure gives the weight of formic acid in 100 g. of fish. This value (mg. per 100 g.) is the "formic acid number." The following figures were obtained with canned mackerel in three stages of decomposition, the first figure being for the fresh, and the third for the badly tainted product:—volatile acid number, 12·3; 21·5; 48·7; formic acid number, 0·82; 1·85; 3·60. With fish packed in sauce containing acetic acid, the volatile acid number is of little value, but the formic acid number may be used as a reliable index of the condition of the sample.

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* Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. No. 647, price 3s. 6d. net, post free 3s. 8d. No. 809, price 2s., post free 2s. 2d.

A. O. J.

Analysis of some North American Indian Food Plants. E. Yanovsky and R. M. Kingsbury. (*J. Assoc. Off. Agr. Chem.*, 1938, 21, 648–665.)—Analyses of 119 food plants belonging to 66 species and 28 natural orders are recorded. All these plants have been used as food by the aboriginal North American Indians. The methods employed are mainly those described in *Assoc. Off. Agr. Chem., Methods of Analysis* (4th Ed., 1935). Sugars were determined by the Munson and Walker method after preliminary preparation of the sample (*op. cit.*, p. 341). Polarimetric readings taken before and after inversion indicated the nature of the sugars present and served for the detection of inulin, which has a negative rotation changed by inversion to a higher negative value. Differences in the determination of starch by the acid and the diastatic methods were recorded as hemicellulose. For liquorice plants crude glycyrrhizin was determined by extraction with alcohol, precipitation with dilute sulphuric acid after the removal of alcohol, purification by solution in ammonia, and re-precipitation with dilute sulphuric acid. Of the 66 species examined, 6 contained inulin as reserve carbohydrate material. These were the bulbs of *Allium nuttallii* S. Wats; the bulbs of *Quamasia spp.* (Camas bulbs); the roots of *Balsamorhiza spp.*; the tubers of *Helianthus tuberosus* L. (Jerusalem artichoke); the roots of *Leontodon taraxacum* L. (dandelion) and the roots of *Wyethia spp.* Lichenin is present as reserve material in *Alectoria jubata* (L.) Ach. Hackberries (*Celtis occidentalis* L.) have an abnormally high calcium-content amounting to 25 per cent. by weight (as calcium carbonate) of the dry fruit. Some foods, *e.g.* the nuts of *Aesculus californica* (Spach) Nutt. (Californian buckeye), which are considered poisonous or obnoxious by white peoples, were made into palatable food by the Indians. Samples of *Glycyrrhiza lepidota* Pursh contained from 7·7 to 14·8 per cent. of crude glycyrrhizin (on dry basis), but none had the sweet taste of the officinal plant, *G. glabra* L. The percentage composition of the ash (4·4 per cent.) of *Glycyrrhiza lepidota* is as follows, the figures in brackets being the corresponding figures for *G. glabra* (ash, 6·2 per cent.):—potassium oxide, 12·9 (18·4); phosphoric anhydride, 8·1 (4·0); calcium oxide, 40·2 (22·4); magnesium oxide, 4·9 (7·1); manganic oxide, 0·025 (0·052); iron and aluminium oxides (mainly iron oxide), 6·1 (11·3). A. O. J.

Analysis of the Fruit and Leaves of *Bauhinia reticulata* D.C. The Presence of Large Quantities of *l*-Tartaric Acid. J. Rabaté and A. Gourévitch. (*J. Pharm. Chim.*, 1938, **28**, 386–397.)—The pericarp of the fruit contains 16 per cent. of a balsam extract soluble in acetone, 1·1 per cent. of reducing sugars, 2·7 per cent. of sucrose and 6 per cent. of pectin. The whole fruit contained 1·4 per cent. of free *l*-tartaric acid and 3·9 per cent. of *l*-tartaric acid as acid potassium tartrate (4·9 per cent. of tartrate) and 1·3 per cent. of K_2O; allowing for the solubility of the tartrate in the mother liquors, the quantity of *l*-tartaric acid in the fruit must be about 6 per cent. The dry leaves contained 1·5 per cent. of free *l*-tartaric acid, 3 per cent. of *l*-tartaric acid as potassium tartrate, and 1·4 per cent. as neutral calcium tartrate. The fruit and leaves of *Bauhinia reticulata* D.C. are the only natural source of *l*-tartaric acid and could easily supply considerable quantities of the material (40 to 50 g. per kg. of dry matter). E. M. P.

Malic Acid in Bordeaux Musts and Wines. E. Peynaud. (*Ann. Falsif.*, 1938, **31**, 332–347.)—Hitherto the proportion of malic acid in wine has had to be determined by difference, but a method is now put forward which depends on the manganic oxidation of a molecule of malic acid to acetaldehyde. The distillation apparatus used carries a capillary funnel which allows a dilute (0·01 *N* or 0·005 *N*) solution of potassium permanganate to fall at the rate of 1 drop per second on to the surface of the boiling solution of malic acid; the acetaldehyde is collected in the distillate. The proportion of malic acid present should be small—about 0·05 to 2 mg.-equivalents (1 mg.-equivalent is 67 mg.). The *p*H of the malic acid solution should be adjusted to about 3·2 with a buffer solution (150 g. of potassium dihydrogen phosphate and 5 ml. of syrupy phosphoric acid per litre). Oxidation, which should be slow, is catalysed by the addition of a few mg. of manganese sulphate. Boiling should be brisk and pumice used to prevent bumping. The acetaldehyde is determined either by the method of Jaulmes and Espezel (*Ann. Falsif.*, 1935, **28**, 325; Abst., ANALYST, 1935, **60**, 703), as already applied by the authors to the determination of lactic acid, acetal, etc., or by titration with iodine in alkaline medium. Ethyl alcohol, and probably its esters, lactic acid, glycollic acid, glycerol in acid medium, and certain sugars yielding formaldehyde may be eliminated by precipitating the malic acid, but at *p*H 3·2 the production of acetaldehyde from substances such as these is almost negligible. Corrections must be made for the production of acetone from citric acid and a small amount of acetaldehyde from tartaric acid, but with musts and wines such corrections are small. With fruits such as peaches, apricots, etc., containing citric and malic acids, both acids may be determined in one oxidation after precipitation. Half the distillate is used for the determination of aldehyde and acetone. In the other half the aldehyde is oxidised with permanganate (0·5 *N* sulphuric acid, 0·1 *N* potassium permanganate solution) at ordinary temperature, the excess of oxidising agent is reduced after 45 minutes with ferrous sulphate, and the acetone (which has not been affected) is separated by distillation and titrated with iodine in alkaline medium, giving the proportion of citric acid; the difference between the two titration figures, corresponding with the acetaldehyde, gives the malic acid. The malic acid in musts and wines is determined as follows:—Ten ml. of the wine or must are neutralised with ammonia solution, diluted to three times its volume, and treated with 5 ml. of *N* barium chloride solution and 60 ml. of 90 per cent. alcohol saturated with barium malate. The mixture is left in a refrigerator for 2 or 3 hours, and the voluminous precipitate (containing all the tartrate and citrate and part of the succinate) is filtered off and washed with two 25-ml. portions of 72 per cent. alcohol saturated with barium malate. It is then transferred with warm water to a beaker, and the mixture is boiled and treated with 5 ml. of *N* sulphuric acid, which liberates the acids. After cooling, the volume is made up to 100 ml., the liquid is filtered, and 10 ml. of the filtrate are used for the oxidation. The liquid is boiled for a few minutes before the oxidation in order to get rid of traces of alcohol. Errors of experiment for artificial wines, musts and wines to which malic acid had been added in varying quantities did not exceed 2 mg.-equivalents per litre. During the progress from grape to non-sulphited wine the proportion of malic acid gradually diminishes during maturation until the zero point may even be reached, but the actual proportion of malic acid found in various vintages differs considerably. Alcoholic fermentation of various musts at 25° C. for 14 days resulted in a loss of about 10–15 per cent. The proportion of malic acid in some of the chief white Bordeaux wines of the years between 1914 and 1937 varied between 3·30 g. per litre in a 1936 wine from Illats, Graves, and 0·28 g. in a 1933 wine from Plassac Blayais; for red Bordeaux wines, from 0·53 g. per litre in a 1935 wine from Pomerol, St. Emilionnais, to 0·00 in a wine of 1926 from St. Julien, Médoc. D. G. H.

Detection of Horse-fat in Admixture with Lard, Beef-fat or Mutton-fat. B. Paschke. (*Z. Unters. Lebensm.*, 1938, **76**, 476–478.)—The method officially recommended in Germany for the detection of horse-fat in the presence of other fats by means of the refractive index and the iodine value is not reliable. The new method depends upon the presence in horse-fat of 1 to 2 per cent. of linolenic acid and its relative scarcity (0·1 per cent.) in the other animal fats. The procedure is an adaptation of that of Rossmann (*Fette u. Seif.*, 1936, **43**, **224**) for the determination of linolenic acid by conversion into its hexabromide. The fat (10 g.) is saponified under reflux (½ hour) with 100 ml. of 0·5 *N* alcoholic potassium hydroxide and, after the removal of alcohol and dilution with water, the soap solution is shaken with about 15 ml. of 5 *N* sulphuric acid, 250 ml. of saturated sodium chloride solution and 50 ml. of ether. The separated ethereal layer is washed three times with salt solution and filtered. A portion (5 ml.) of the filtrate is cooled to −15° C. in an ice-and-salt mixture simultaneously with 5 ml. of pure ether. Bromine (0·45 ml.) is added from a burette to the cooled pure ether, and this solution is added gradually in five or six portions to the fatty acid solution, the temperature being kept below 0° C. The mixture is allowed to remain in the freezing-mixture for ten minutes, and then left at 5° to 10° C. for 15 to 18 hours. Before filtration of the precipitated hexabromide, the mixture is allowed to stand for a short time in a warm room at 13 to 15° C. in order that any precipitated free fatty acids may be re-dissolved. The precipitate is collected in a weighed filter-tube (Allihn) and washed twice with 3 ml. of ether cooled to −10° C., and it is important that the precipitate should remain covered with liquid during the filtration and washing. The precipitate is dried at 100° C. and, when cold, is again washed at room temperature with 5 ml. of ether. (The hexabromide is less soluble in ether when dry than when freshly precipitated.) Finally the precipitate is dried at 100° C. and weighed. The amounts of hexabromide yielded by 1 g. of fat were:—horse-fat, 41·2 mg.; lard, 2·8 mg.; beef-fat, 3·0 mg.; mutton-fat, 3·3 mg. When mixed with 30 per cent. of horse-fat the other fats yielded (mg. per g.):—lard, 8·2; beef-fat, 10·8; mutton-fat, 11·0.

A. O. J.

Fatty Acids in the Lecithin and Glyceride Fractions of Egg-yolk. R. W. Riemenschneider, N. R. Ellis and H. W. Titus. (*J. Biol. Chem.*, 1938, **126**, 255–263.)—An examination by the usual methods was made of the fatty acids of the lecithin and glycerides of egg-yolk. The findings of previous workers were substantially confirmed, except that the evidence indicated the presence of clupanodonic acid rather than of arachidonic acid, and that no evidence was obtained of the presence of isopalmitic and margaric acids. The following table shows the composition of the lecithin and glyceride fatty acids:

	Lecithin fatty acids		Glyceride fatty acids	
Acid	Per cent. by weight	Molecular per cent.	Per cent. by weight	Molecular per cent.
Myristic	—	—	0·7	0·8
Palmitic	31·8	34·6	25·2	27·0
Stearic	4·1	4·0	7·5	7·3
Palmitoleic	—	—	3·3	3·6
Oleic	42·6	42·0	52·4	51·0
Linolic	8·2	8·2	8·6	8·4
Clupanodonic	13·3	11·2	2·3	1·9
Total saturated	35·9	38·6	33·4	35·1
,, unsaturated	64·1	61·4	66·6	64·9

F. A. R.

Composition of the Wax-like Substance Extracted from the Coffee Berry. Part II. H. Wagner. (*Z. Unters. Lebensm.*, 1938, **76**, 449–475.)—In continuation of the previous work (*Z. Unters. Lebensm.*, 1938, **76**, 1; Abst., ANALYST, 1938, **63**, 667), other methods for the separation of the constituent fatty acids of this substance have been investigated. Meyer and Eckert have reported the possibility of separating the individual acids by differences in the solubilities of their methyl esters. The petroleum spirit extract of the wax was saponified with lithium hydroxide and the mixed acids obtained by decomposition of the lithium salts were converted into their methyl esters. These esters were separated into fractions according to their solubilities in methyl alcohol, and the fatty acids obtained from them by saponification were purified by recrystallisation from glacial acetic acid and other solvents. Further separations of these acids were effected by precipitation with lithium acetate or conversion into their lead salts. Fractions of approximately equal m.p. were united and further separations were made by similar methods. By another method the petroleum spirit extract of the wax was esterified directly by heating with methyl alcohol and sulphuric acid under reflux and the esters were subsequently extracted with ether. The purified esters were fractionally distilled *in vacuo*. By a third method the original wax was saponified with alcoholic potassium hydroxide solution in the presence of toluene. The fatty acids obtained by decomposition of the soap were converted into their methyl esters which were fractionally distilled *in vacuo*. The various fractions of mixed fatty acids obtained by these methods were investigated. According to Meyer and Eckert the solid fatty acids contain capric, daturic, palmitic and carnaubic acids; according to Heiduschka and Kuhn (*J. prakt. Chem.*, 1934, **139**, 270), capric, palmitic, stearic and carnaubic acids, and according to Bengen and Anderson (*J. Biol. Chem.*, 1932, **97**, 99; Abst., ANALYST, 1932, **57**, 579) palmitic, stearic and carnaubic (but not capric) acids. By investigation of the behaviour of capric acid and its salts in the presence of other acids, a method was devised whereby capric acid, if present in the mixture of fatty acids, could be detected. Capric acid was not detected in any of the appropriate fractions. From certain of the fractions of the esters separated by distillation *in vacuo* a fatty acid fraction was finally obtained which corresponded with the "daturic acid" of Meyer and Eckert, and which could not be separated further by precipitation with lithium acetate. Although this fraction simulated a single substance it was proved to be a mixture separable by fractional precipitation with magnesium acetate into palmitic acid and an acid of higher molecular weight. By fractional precipitation of mixed acid fractions of m.p. above 60° C. in the form of their lithium salts, pure palmitic acid was isolated and identified. Methods designed to isolate stearic acid, if present, were not successful, but evidence was obtained of the presence of an acid of approximate molecular weight 310 to 314 which resembled arachidic acid. A. O. J.

Extractives and Mineral Matter in Chicory. L. Hoton. (*J. Pharm. Belg.*, 1938, **40**, 760–762; 777–780.)—An extensive investigation has been carried out to determine if any modification is advisable of the limits fixed in Belgium for mineral matter (maximum 10 per cent.) and hot-water-soluble extractives (minimum 60 per cent.) of chicory, *Cichorium intybus*. Before limits can be fixed for chicory as sold, the composition and variations in the original root and the industrial processes concerned in the preparation must be taken into account. The fresh root contains about 75 per cent. of water, and in the drying process loses about 75 per cent. in weight; in the roasting process the dried product loses about 25 per cent. in weight. Published figures for the ash of roasted chicory vary from

3 to 5 per cent., averaging about 4·5 per cent., which means about 1 per cent. on the original root. Washing and drying of the root does not remove every particle of adherent soil. A classification of the cut root according to size with the proportion of mineral ash commonly found in each (*Rapport du Syndicat français des Fabricants de Chicorée*) is as follows:—Cossettes, "grosses" 50–52 per cent. of the roots, with ash 7–8 per cent.; "moyennes," 10–15 per cent., ash 7–8; "fines," 25–30 per cent., ash 7–9. The remainder, called "touraillons," is further classified according to size—"gros," 2–3 per cent., ash 8–10 per cent.; "moyens," 1–2 per cent., ash 10–12 per cent.; "fins," 1 per cent., ash 15–25 per cent., "pellicules," 1–2·5 per cent., ash 35–45 per cent. Normal industrial cossettes, however, never have an ash over 6 per cent., nor the next grade, over 7 per cent. Much of the extraneous mineral matter from the soil will be separated during drying and roasting, and sieving or winnowing will remove it. From a study of factory conditions 8 per cent. of ash is regarded as a maximum, and there should be no difficulty in keeping below it. In the manufacture of chicory extract in the form of powder most of any extraneous mineral matter will pass into the powder, but if all the adherent soil is previously removed the ash of the powder will not exceed that of the original root. An actual experiment gave the following percentages of ash; cossettes, 4·8; "grosse semoule," 4·3; "moyenne semoule," 4·4; "petite semoule," 4·5; powder, 5·6 per cent. The proportion of extract in hot water is at present fixed in Belgium at a minimum of 50 per cent., but this is regarded as too low, since the roasting, which raises the proportion of soluble matter, can easily be adjusted to give a product with 60 per cent. of soluble matter. Ordinarily, chicory sold in Belgium is not allowed to contain more than 15 per cent. of water.

D. G. H.

Determination of Cocaine in Coca Leaves. A. W. K. de Jong. (*Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 1218–1222.)—A method of extracting cocaine from its 0·1 *N* hydrochloric acid solution is suggested, which differs somewhat from that published in the *Bulletin of the Health Organisation of the League of Nations* (*cf.* ANALYST, 1938, **63**, 828). Instead of neutralising the 45 ml. of the acid solution with 1 g. of sodium bicarbonate and then shaking three times with 30 ml. of a mixture of 2 parts of ether and 1 part of light petroleum, it is proposed to neutralise the solution with 5·5 ml. of *N* sodium carbonate solution and extract three times with 30 ml. of ether. This makes the extraction more rapid and avoids the use of the mixed solvent. On adding sodium bicarbonate to a solution of cocaine hydrochloride, no precipitate is formed, for the cocaine remains in solution as its bicarbonate. Such a solution tends to lose carbon dioxide, with the formation of free cocaine. Extraction of such a solution with ether disturbs the equilibrium and leads to more or less complete dissociation of the bicarbonate. By adding sufficient sodium carbonate, however, the free bases are at once liberated and can thus be extracted much more rapidly and completely than by the use of bicarbonate. Unfortunately, other bases such as hygrines and amino-acid esters are also extracted under these conditions, which leads to high results. Correct results can be obtained by re-dissolving the bases in hydrochloric acid and again neutralising and extracting with ether. To avoid the necessity for this re-treatment or, alternatively, the application of a correction, an amount of sodium carbonate has been deliberately chosen "by which a quantity of bases is obtained equal to that of the cocaine." This condition is satisfied by adding 5·5 ml. of *N* sodium carbonate solution to the 45 ml. of cocaine solution. F. A. R.

***Semen Strychni*. E. Le Coultre and P. Van der Wielen.** (*Pharm. Weekblad*, 1938, **75**, 1329–1332.)—The dimensions specified for *Semen Strychni* (Nux vomica) by Pharmacopoeias representing 17 nations and by other authorities, are compared. The diameter is usually given as 2·0 to 2·5 cm., but figures of 1·0, 1·5 and 3·0 occur in some instances. The value for the minimum thickness is usually 0·3 cm. and the maximum 0·5 cm., but in some specifications dimensions up to 0·5 cm. and approximately 0·5 cm. are specified, whilst one Pharmacopoeia (Austria, 1906) does not specify any value at all. Tschirch (*Handbuch der Pharmakognosie*, 1923, Vol. III, p. 450) states that the diameters vary according to the origin of the seeds; thus, values for Bombay seeds range from 2·0 to 2·2; Cochin, 1·9 to 2·8; Madras, 1·2 to 2·1; Ceylon, 1·3 to 2·5; Malabar, up to 3·4 cm. (thickness, 5 to 6 mm.). Data are given for a large number of commercial samples of the seeds, which were divided according to size into large, medium and small grades. The respective average diameters were 2·20, 1·80 and 1·52; weight, 1·731, 1·181 and 0·820 g.; fat-content, 5·62, 6·27 and 6·6 per cent.; alkaloid-content (determined by the method of the Dutch Pharmacopoeia, 5th Ed.), 2·62, 2·82 and 2·88 per cent.; brucine and strychnine in the alkaloids (determined by the method of the Dutch Pharmacopoeia Commentary, Pt. IV, p. 129), 0·86, 0·91 and 1·02 per cent. (all percentages being calculated on the dry substance). These last figures are lower than those given in the Dutch Pharmacopoeia, although, according to the literature, the strychnine-content may fall within the range 0·54 and 1·54 per cent. Only the U.S., British and Brazilian Pharmacopoeias specify minimum strychnine-contents (1·15, 1·2 and 1·25 per cent., respectively), but no mention is made of brucine, which is associated with strychnine, but is much less toxic. A minimum strychnine-content of 1 per cent. is to be expected. J. G.

***Senecio vulgaris* (and its Pharmacological Properties). J. Van der Meer.** (*Pharm. Weekblad*, 1938, **75**, 1169–1177.)—Although *Senecio vulgaris* (common groundsel) has recently been introduced for treating uterine troubles, the nature of the active principle responsible for its effects is not known. Existing work comparing the nature and effects of the alkaloids present in the different varieties of *Senecio* is summarised. In the months of April and September the only alkaloid found in *S. vulgaris* is senecionine, $C_{18}H_{25}O_5N$, although other alkaloids are present during the summer months. Varieties of *Senecio* found around London (*viz. S. vulgaris* and *S. jacobaeae*) are not toxic, but these same varieties from New Zealand and S. Africa have been known to cause wasting, sickness, gastric haemorrhage, diarrhoea, cirrhosis of the liver, and even death when eaten by cattle. *S. jacobaeae* contains the alkaloid jacobine, $C_{18}H_{23}O_5N$. *S. latifolius* contains the alkaloids senecifoline, $C_{18}H_{27}O_8N$, and senecifolidine, $C_{18}H_{25}O_7N$, and in small quantities it produces haemorrhagic effects, especially on the liver; larger quantities affect the central nervous system. *S. silvaticus* (which contains the alkaloid silvasenecine, $C_{18}H_{21}O_4N$) acts similarly, whilst *S. illicifolius* and

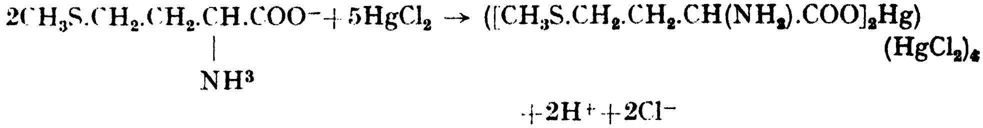
S. burchelli have found their way into bread for human consumption, and have then caused diarrhoea and vomiting with loss of blood, and emaciation. The pharmacological experiments were carried out by comparing the effects of extracts and decoctions of powdered *Radix Senecionis vulgaris* on the horn of an isolated uterus weighing 250 to 300 g. with that of a standard preparation of histamine; the Storm van Leeuwen technique was used. Subsequently a standardised extract of *S. vulgaris* was used to check the histamine, and so to eliminate any change in its activity. Approximately 2 ml. of an extract in water was equivalent in its effect to 1 ml. of a 0·002 per cent. solution of the histamine; the small quantity of nipagin used as a preservative was shown to have no influence on the results. A decoction in water was less effective than the extract. Although alcohol inhibits the test, its effect is negligible compared with the reverse effect exerted by alcoholic extracts of *S. vulgaris*. Thus an extract in 30 per cent. alcohol was 25 per cent. more effective than the extract in water, the extracts in 70 and 90 per cent. alcohol being both approximately 100 times more effective than the 30 per cent. extract. An extract of *Radix S. jacobaeae* in 70 per cent. alcohol was more effective than a similar extract of *Radix S. vulgaris*; extracts of *Herba S. jacobaeae* and *Radix S. jacobaeae* were similar in effect; *Herba S. vulgaris* was much weaker in its action. The action on the heart of a frog was then tested; the aqueous extract acted powerfully, the extract in 70 per cent. alcohol being much weaker. Attempts were made to isolate the constituent responsible for the action on the uterus. The extract in 70 per cent. alcohol was acidified with hydrochloric acid, diluted with an equal volume of water, evaporated to its original volume (to remove the alcohol) and filtered. The residue from the filtration was washed with acidified water, which left a green mass, consisting mainly of the hydrochlorides of the alkaloids. It was made alkaline with ammonia and extracted with chloroform (until Bouchardat's reagent gave a negative reaction for alkaloids in the aqueous layer), and the chloroform was removed by evaporation. Although a solution in alcohol of the green mass gave an active uterus test equivalent in activity to that of the original extract, the solution remaining after extraction with chloroform and a solution of the alkaloid hydrochlorides in water were inactive. The green mass had a characteristic odour which was removed by steam-distillation, and the resulting distillate gave an active uterus test. The distillate was salted-out and extracted with ether, and the extract on evaporation left a white solid which was inert towards the uterus, although the residue of the green mass was active. Solutions of the green mass in various alkalis were also tested, but gave negative results; this may have been due to the inhibiting action of the alkali. Solutions prepared from other organic solvents, or by heating, were also inactive. When the solution of the green mass in alcohol was decolorised with activated carbon it yielded a liquid which, on evaporation, proved very active; treatment with silica gel or diatomaceous earth was less effective. Dilution with water produced a precipitate; this was extracted with ether, the extract was dried with anhydrous sodium sulphate, and the residue left on evaporation was dissolved in alcohol; the solution was very active. The solution remaining from the extraction with ether was extracted with chloroform, and a solution of the residue left on evaporation of the solvent was found to be inactive, as was also the aqueous solution remaining after extraction with chloroform. When a solution of the green mass in alcohol was diluted with water and extracted with ether, the extract was more easily decolorised than the original solution and, when dried and evaporated under reduced pressure, yielded a colourless viscous liquid. A similar product was obtained by extracting the original *Radix Senecionis vulgaris* with 70 per cent. alcohol, and then extracting the diluted and acidified extract with petroleum spirit. This new extract, when decolorised and evaporated, yielded 2·3 g. of a viscous pale yellow liquid (n_D^{20} 1·4830, setting p. 11° C.) from 5 kg. of the original preparation. It had a characteristic odour, was insoluble in water and most organic solvents, and contained 79·09 per cent. of carbon and 11·37 per cent. of hydrogen. Nitrogen, halogens, sulphur and phosphorus were absent, but tests for unsaturated carbon linkages and aromatic aldehyde groups were positive. The pharmacological strength was more than double that of histamine. J. G.

Biochemical

Study of Sulphaemoglobin. H. O. Michel. (*J. Biol. Chem.*, 1938, **126**, 323–348.)—Sulphaemoglobin, with an absorption band at 620$m\mu$, is formed by treating a solution of haemoglobin with sodium hydrosulphite solution, adding a drop of ammonium sulphide solution, and then a drop of hydrogen peroxide solution. Sodium perborate, or any other substance yielding hydrogen peroxide in water, can be used instead of hydrogen peroxide. Other oxidising agents, such as potassium ferricyanide, potassium chlorate, potassium permanganate or bromine, fail to produce sulphaemoglobin. In the same way sulphide sulphur is essential for the formation of sulphaemoglobin, other forms of sulphur, such as thiourea, cystine, thiosulphate, sulphite or elementary sulphur, being without action. The solubility, resistance to alkali, molecular weight and cataphoretic mobility of sulphaemoglobin are not appreciably different from those of haemoglobin. It can be prepared from artificial haemoglobins containing porphyrins other than protoporphyrin, so that the latter possesses no special structure essential to its formation. One atom of sulphur for each atom of iron present is necessary in the conversion of haemoglobin into sulphaemoglobin, and the latter contains one atom of sulphur easily oxidisable by bromine to sulphate; this sulphur is not present as a free sulphydryl group. Sulphaemoglobin combines with carbon monoxide, one molecule of the latter being bound for each atom of iron present. Reduced sulphaemoglobin is very stable, but the oxidised form is unstable. A sulphaemoglobin can also be prepared from muscle haemoglobin; this has a greater specific absorption than blood sulphaemoglobin and is more stable; it also forms a carbon monoxide compound.

It is suggested that the condition of sulphaemoglobinaemia depends on the formation of hydrogen sulphide in the organism together with the administration of acetanilide or related derivatives. Although *in vitro* neither acetanilide nor aniline is capable of catalysing the formation of sulphaemoglobin from oxyhaemoglobin and sulphide, *p*-aminophenol, which has been shown to be formed from acetanilide in tissues, can do this. It is readily autoxidisable to a quinone form, with the formation of hydrogen peroxide; this is probably the active agent in producing sulphaemoglobin. F. A. R.

Reaction of Methionine and other Amino Acids with Mercuric Chloride. G. Toennies and J. J. Kolb. (*J. Biol. Chem.*, 1938, **126**, 367–379.)—The factors governing the precipitation of methionine with mercuric chloride were studied. The substances appear to react according to the equation:



$$2CH_3S.CH_2.CH_2.\underset{\displaystyle NH^3}{\underset{|}{CH}}.COO^- + 5HgCl_2 \rightarrow ([CH_3S.CH_2.CH_2.CH(NH_2).COO]_2Hg)(HgCl_2)_4 + 2H^+ + 2Cl^-$$

free acid being formed corresponding to one equivalent per molecule of methionine. Complete precipitation was favoured by neutrality, by the absence of chloride ion, by the removal with mercuric acetate of free chloride ion formed in the reaction, and by the presence of alcohol. Basic amino-acids, which form precipitates with mercuric chloride, and acid amino-acids, which form precipitates with the mercury ion of mercuric acetate, interfere with the precipitation of methionine. Neutral amino-acids do not interfere by precipitate formation, but they react with mercuric chloride to form soluble compounds, probably thus:

$$R(NH_3^+)COO^- + HgCl_2 \rightarrow R(NH_2)COOHgCl + H^+ + Cl^-$$

Consequently an excess of mercuric chloride must be added to compensate for that required by this reaction, and also mercuric acetate and alkali to remove the chloride ion. F. A. R.

Occurrence of Nicotinic Acid in Ox-liver. D. Ackermann and H. G. Fuchs. (*Z. physiol. Chem.*, 1938, **256**, 90–94.)—The presence of nicotinic acid in liver, reported by previous workers, has been confirmed by the isolation of the acid in a quantity (0·85 g. from 69 kg. of liver) adequate for a detailed examination to be made. Analyses of the free acid and of its flavianate gave figures in close agreement with the theoretical values. Moreover, the acid had the same m.p. and crystalline form, and gave the same characteristic colour reactions as nicotinic acid. It gave no depression in m.p. with an authentic specimen. The method employed in isolating the acid did not involve any stages sufficiently drastic to have hydrolysed any nicotinamide present, and it therefore seems unlikely that the acid was derived from amide. Neither trigonellin nor betaine could be detected in the appropriate liver fractions, and it seems equally unlikely that either of these could be the precursor of nicotinic acid. It is concluded that the acid is derived from the food, and is stored as such in the liver. F. A. R.

Antirachitic Provitamin from Wheat-germ Oil. A. Windaus and F. Bock. *Z. physiol. Chem.*, 1938, **256**, 47–48.)—The provitamin D content of wheat-germ oil sterols was increased from 1·2 to 85 to 90 per cent. by repeated chromatographic adsorption on alumina and elution. The provitamin was identified as ergosterol by a mixed m.p. determination and analysis of its acetate and 3:5-dinitrobenzoate, and by the mixed m.p. of the following derivatives with the respective authentic specimens:—α-dihydroergosterol and its acetate, α-ergostenol and its acetate, ergopinacone and its acetate. The irradiated provitamin possessed the biological activity of irradiated ergosterol and not of irradiated 7-dehydro-sitosterol or 7-dehydrostigmasterol. F. A. R.

New Vitamin D in Cod-liver Oil. C. E. Bills, O. N. Massengale, K. C. D. Hickman, and E. Le B. Gray. (*J. Biol. Chem.*, 1938, **126**, 241–244.)—The most volatile antirachitically-active fraction of cod-liver oil, prepared by molecular distillation, was assayed for vitamin D on both rats and chickens. Rat unit for rat unit, this fraction was only one-half to one-quarter as effective for chickens as the total vitamin D of cod-liver oil. This evidence supports the hypothesis formulated to explain the results obtained by molecular distillation, *viz.* that several vitamins D exist in cod-liver oil. F. A. R.

Toxicological and Forensic

Action of Nicotine on the Human Organism. W. Brandt. (*Chem.-Ztg.*, 1938, **62**, 851–852.)—The fatal dose of nicotine is not known with certainty, but 2 to 3 drops (30 to 60 mg.) of the pure alkaloid will cause death to man, whilst if a glass rod is dipped in nicotine and held under the beak of a bird, death will result in a few seconds. The tolerance of a moderate but habitual smoker towards nicotine in the form of vapour is 16 to 20 mg. per hour. Although 5 g. of tobacco (*i.e.* one average cigar or 5 cigarettes) contain about 60 mg. of nicotine, only about 10 and 40 per cent. of this, respectively, are evolved with the smoke, and only 20 per cent. of this fraction finds its way into the system, except perhaps when the smoke is inhaled, when the percentage may rise to 80. The actual amount of nicotine entering the system will vary considerably with the method of smoking and the type of tobacco (*e.g.* from 1·2 to 19 mg. from 5 g. of the original tobacco), but a normal figure appears to be 8 mg. or less per hour, and apparently this produces no manifest symptoms of nicotine poisoning. Such symptoms include an increase in blood-pressure, catarrh of the throat and larynx, heart and eye troubles and possibly, gastric ulcers and diuresis. Thus the urine excreted by a female occasional smoker in 3 hours was increased from 340 to 975 ml. as the result of smoking one cigarette 30 minutes before the first sample was taken, whilst a male habitual smoker was unaffected under similar conditions. From the point of view of effects on the human organism, nicotine is the most important constituent of tobacco. Cigars and cigarettes are roughly equivalent in this respect, because inhalation is more customary with cigarettes and they are smoked in larger numbers. Cigars can contain up to 3·5 per cent. of nicotine, cigarette tobacco contains on an average 1 to 2 per cent., and "low-nicotine" brands of cigars 0·6 to 1·0 per cent. The saliva and other body fluids that come into contact with tobacco smoke cause the suspended particles to be deposited, so that the nicotine is more easily carried into the system. An irritant effect on the mucous membrane also results, although this is not attributed to the nicotine present. Attempts to remove nicotine from tobacco smoke (*e.g.* by means of wads of cotton wool or of tannin or silica gel filters in the end of the cigarette) or to remove it from (*e.g.* by extraction) or fix it in the tobacco beforehand have not proved entirely satisfactory, either because the reduction in nicotine-content is insignificant, or because the flavour and aroma of the tobacco are affected. More promising results may be expected from experiments which are being carried out on the breeding of strains of tobacco plant which have low nicotine contents (*cf. ibid.*, 1938, **62**, 841;

and Wenusch, *Z. Unters. Lebensm.*, 1934, **68**, 412; 1937, **74**, 492, 497; *cf.* ANALYST, 1927, **52**, 728; 1929, **54**, 164; 1931, **56**, 753; 1932, **57**, 181, 727; 1933, **58**, 44, 165, 625; 1935, **60**, 260, 829). J. G.

Technique for the Determination of Alcohol in Blood. Anon. (*Chem.-Ztg.*, 1938, **62**, 852.)—In the determination of alcohol in blood by Widmark's method (*cf. Biochem. Z.*, 1922, 407, 473; "*Pharmakol. Beiträge z. Alcoholfrage,*" Pharmakol. Inst., Jena, 1938, Vol. 8) the potassium dichromate solution used should not only be stored in the dark, but also prepared and used in the dark. The distillation flask should be filled in a darkened room, and the titration should be carried out with only the titration flask illuminated, the daylight lamp of the Pulfrich photometer being suitable for this purpose. The temperature should be controlled by means of a thermostat, and not by a water-bath as suggested, and it should not exceed 50° C., as the titre of the potassium dichromate solution then varies considerably. Details of technique for the transference of the sample to the distillation-flask are also given; the outlet of the apparatus should be carefully cleaned with a mixture of potassium dichromate and conc. sulphuric acid and thoroughly washed, and the formation of bubbles should be avoided. When a series of determinations is being made the titrations should be carried out, so far as possible, in rapid succession, and each titration should take less than 1 minute. The potassium iodide solution should be colourless (as a yellow colour indicates the presence of free iodine), and the determinations should be made only by practised workers. Maximum, minimum and average "fasting values" recorded for the alcohol-content of blood are 0·05074, 0·0029 and 0·0286 parts per thousand, respectively. J. G.

Identification of Traces of Alcohol. Determination of Alcohol in Urine. J. M. Hambersin. (*J. Pharm. Belg.*, 1938, **20**, 741–746.)—The iodoform and oxidation methods for the determination of alcohol are not specific, particularly when blood or urine is being examined. A modification of Rosenthaler's method (*Chem.-Ztg.*, 1912, **36**, 830; *Z. anal. Chem.*, 1914, p. 196; Abst., ANALYST, 1912, **37**, 407) is preferred because, although it determines all primary alcohols, the colour obtained from methyl alcohol is negligible in intensity, and it is unlikely that alcohols containing more than 3 carbon atoms will be found in urine. Four ml. of a solution of 1 g. of sulphanilic acid in a mixture of 150 ml. of water and 50 ml. of 0·2 *N* hydrochloric acid, are mixed with 1 ml. of a 0·7 per cent. aqueous solution of sodium nitrite. One ml. of a 0·5 *N* solution of sodium hydroxide and then 1 ml. of the sample are added and the mixture is warmed; in the presence of alcohol a blood-red colour develops. The alcohol is oxidised by the diazo-compound, which reacts with the aldehyde so formed to produce the red compound, the chemical nature of which is not known. The colour is matched against standards prepared from solutions containing known amounts of alcohol, allowance being made for a blank determination. As the colour is unstable it must be developed simultaneously in the standards and sample. If urine is to be examined, 100 ml. are distilled in a small flask having a side-tube; the first 10 ml. of distillate are collected, and 1 ml. of this is treated as described above. Experiments have shown that distillation is essential in order to avoid errors due to the colour of the urine or to interference by other substances present in it; and that urine free from alcohol then gives negative results. In test experiments in which known quantities of alcohol were added to urine it was found that with concentrations ranging from 0·8 to 0·008 g. per 100 ml., the whole of the alcohol was obtained in the first 10 ml. of the distillate, and that the method was sensitive to 8 mg. of alcohol per 100 ml. of urine. Curves show the relationship between the amount of alcohol found in the urine and the time that elapses after consuming 10 to 75 ml. of 94 per cent. alcohol. It is concluded that the alcohol-content of the blood or urine is unreliable by itself as an indication of drunkenness; factors such as the age and physical condition of the subject and the concentration of the alcohol absorbed must also be taken into account. J. G.

Bacteriological

Essentiality of Gallium to the Growth and Reproduction of *Aspergillus niger*. R. A. Steinburg. (*J. Agric. Res.*, 1938, **57**, 569–74.)—The effect of traces of gallium on the growth of *Aspergillus niger* has been investigated, special precautions being taken to prevent contamination with other elements. Transparent quartz vessels were used, and the distilled water for the culture medium was distilled successively in an Acree metal still, a Pyrex glass still and a transparent quartz still. The sucrose, which contained only 0·0014 per cent. of ash, was purified by extraction with 95 per cent. alcohol for 6 hours, and the chemicals used were spectroscopically pure. The fungus was grown on 5 per cent. sugar solution to which all necessary salts had been added in approximately optimum concentrations. Each litre contained the following ingredients: sucrose 50 g. ammonium sulphate 3·4 g., potassium dihydrogen phosphate 0·55 g., magnesium 0·025 g., iron 0·2 mg., zinc 0·2 mg., copper 0·05 mg., manganese 0·025 mg., and molybdenum 0·02 mg. Inoculation was made with a spore suspension and, after incubation at 37° C. for 4 days, the mycelial felts were filtered off on 1G3 Jena glass filters, dried overnight at 103° C. and weighed. The experimental results are given in tables. Experiment 1 showed a maximum yield of 847·1 mg. under conditions apparently optimum, whereas with unextracted sugar and reagent chemicals the yield was usually approximately 1150 mg. Tests with the salts of 77 elements led to the selection of gallium as the element capable of eliminating the decrease in yield most effectively, the addition of only 0·02 mg. of this element per litre resulting in a weight of 1123 mg., or almost maximum yield. The tables also record the effect of omitting the elements iron, zinc, copper, manganese and molybdenum. The omission of zinc and manganese had the most pronounced effect, the omission of copper had a medium effect, and that of iron or molybdenum only a slight effect. The conclusion is drawn that, in addition to iron, zinc, copper, manganese and molybdenum, the element gallium at concentrations of 0·01 to 0·02 mg per litre is essential to the growth and reproduction of *Aspergillus niger* in the medium described above. D. R. W.

Light as a Factor in the Production of Pigment by Certain Bacteria. J. A. Baker. (*J. Bacteriology*, 1938, **35**, 625–31; *Bull. Hyg.*, 1938, **11**, 907.)—In order to encourage pigment production it is customary to incubate the culture in the usual way and then to leave it on the bench exposed to diffused daylight. The author has studied the conditions governing the effect of light on the production of pigment, observations being made on an acid-fast saprophytic bacillus producing a pink pigment. He exposed fully-developed cultures to various types of light for different periods and then kept them in the dark and noted the pigment production. He found that exposure of the cultures to sunlight for 15 minutes, to a 100 watt Mazda incandescent lamp at 2 feet distance for 30 minutes, and to a mercury vapour lamp at 3 inches distance for 1 minute caused them to develop maximum pigmentation within 48 hours; the best results were obtained when the cultures were exposed at 37° C. and afterwards kept at 24° to 37° C. He concludes that the production of pigment is a metabolic phenomenon, for cultures killed by exposure at 60° C. for 30 minutes develop no pigment, nor do cultures exposed to light so long as to be killed, and exposure of an alcoholic extract of the unpigmented culture (the pigment in his experiments being readily soluble in alcohol) to light did not lead to pigment formation. D. R. W.

Organic

Simplified Procedure for Analytical Oxime Formation with Aldehydes and Ketones. S. Sabetay. (*Bull. Soc. Chim.*, 1938, 5, 1419–1422.)—For use in the analysis of perfume ingredients, when an accuracy of 95 per cent. is sufficient, the author recommends the following methods, in each of which use is made of a reagent prepared by dissolving 50 g. of hydroxylamine hydrochloride in 90 ml. of hot water, adding 20 ml. of bromophenol blue solution and making up to a litre with 90 per cent. alcohol. The indicator is prepared by grinding 0·1 g. of bromophenol blue with 3 ml. of *N*/20 sodium hydroxide solution and making up to 25 ml. with water; methyl orange may be used instead of bromophenol blue. In each titration the colour should be compared with that of a standard containing one or two drops of *N*/2 potassium hydroxide solution. (*Cf.* S.P.A. Method, ANALYST, 1932, 57, 773; 1934, 59, 105).

Carbonyl compounds that combine with hydroxylamine hydrochloride in the cold.—Exactly 1 g. of fine calcium carbonate, 0·5 to 5 g. of the carbonyl compound or essential oil, and 25 ml. of the reagent are allowed to stand in the cold for 1 to 3 hours, with occasional shaking, in a 150-ml. flask. A control is similarly treated. To each is added 25 ml. of *N* hydrochloric acid, and the liquids are titrated, immediately after the decomposition of the calcium carbonate, with *N*/2 potassium hydroxide solution, a standard indicator colour being used for comparison. The results are calculated from the formula: Percentage of aldehyde = molecular weight × (ml. of KOH for sample − ml. of KOH for control) / (20 × weight taken). The initial acidity can be neglected.

Carbonyl compounds that form oximes with difficulty in the cold.—With compounds such as pulegone and camphor, oxime formation in the cold gives low values, and the reaction must be effected by heating on a boiling water-bath for 1 hour, in the presence of calcium carbonate, by the method of Vandoni and Desseigne (*Bull. Soc. Chim.*, 1935, 2, 1685; Abst., ANALYST, 1935, 60, 776); a control must be used. After cooling, 25 ml. of hydrochloric acid are added, and the titration is carried out as for compounds which react in the cold.

E. M. P.

Inorganic

Electrolytic Determination of Antimony. S. L. Jovanovitch. (*Z. anal. Chem.*, 1938, **114**, 415–425.)—Antimony can be deposited from its solution in strong (*e.g.* 1:1) sulphuric acid, as shown by Sand (ANALYST, 1908, **33**, 411). In more dilute acid precipitation occurs owing to hydrolysis of the normal sulphate, but it has now been found that this does not prevent quantitative deposition of the antimony under suitable conditions. The metal sample (*e.g.* 1 g. or less) is dissolved in 12 ml. of hot conc. sulphuric acid. The cooled mass is dissolved in a little water, and gradually diluted to 150 ml. The suspension of the precipitate formed by hydrolysis of the normal sulphate is warmed to 85° to 90° C., agitated mechanically, and electrolysed at 2·4 volt with a current of 3 amp. In about 20 minutes the precipitate dissolves, and the voltage is then reduced to 2·2, the current decreasing to 0·3 amp. The precipitation is complete at this stage, but the electrolysis is continued for another 30 minutes, the total time taken varying from 60 to 75 minutes. The light grey deposit is washed twice with water and once with alcohol during brisk agitation, dried at 80° to 90° C. for 10 minutes, and weighed. Tartaric acid, even in excess of that present in tartar emetic, was found not to interfere with the deposition. Antimony sulphide obtained by the usual methods is boiled with sulphuric acid, and the resultant solution is electrolysed; native antimony sulphide can be treated in the same manner. The results by this method were found to give an average negative error of 0·1 per cent. of the amount of metal present. W. R. S.

Determination of Arsenic, Antimony and Tin in Alloys. J. A. Scherrer. (*U.S. Bureau of Standards J. of Research*, 1938, **21**, 95–104.)—*Lead base alloys* are dissolved in nitric acid with addition of hydrofluoric acid to obtain complete solution, and the lead is precipitated as sulphate. The filtrate is freed from hydrofluoric and nitric acids by evaporation with sulphuric acid. *Tin-antimony alloys* are attacked with nitric acid, which is displaced by sulphuric acid. *Copper-base alloys* are attacked with nitric acid, the precipitate of stannic and antimonic oxides being collected and dissolved in sulphuric acid. In every instance the sulphuric acid is diluted somewhat, hydrochloric acid is added, and the solution is transferred to a special all-glass distilling apparatus provided with a thermometer well and connected with a carbon dioxide supply. Arsenic, antimony and tin are separated by fractional distillation and caught in separate receivers, the distillates being titrated. The paper is too detailed for abstraction, and should be consulted for working details. W. R. S.

Separation of Cobalt and Nickel from Manganese. E. A. Ostroumov and G. S. Maslennikova. (*Zav. Lab.*, 1938, **7**, 267–269.)—*Method.*—A neutral solution (about 200 ml.) of the chlorides of these metals is treated with pyridine hydrochloride (prepared by diluting 5 ml. of hydrochloric acid, sp.gr. 1·19, with 20 to 25 ml. of water and neutralising with pyridine, methyl red being used as indicator). The solution is heated to boiling, 5 to 10 ml. of 20 per cent. pyridine solution are added, and hydrogen sulphide is passed in for 10 to 15 minutes, with shaking. The cobalt and nickel sulphides are filtered off and washed with hydrogen sulphide water containing a few drops of pyridine. Manganese is precipitated from the filtrate as manganese ammonium phosphate and determined as the pyrophosphate. Tests with solutions containing known amounts of manganese and either cobalt or nickel indicated that the separation was complete. In solutions containing known weights of the three metals, determination of manganese by a colorimetric method in the precipitate of mixed nickel and cobalt sulphides showed none, or only faint traces. The method can be used with very various products, *e.g.* metals, ores, and various catalysts used industrially.

Remarks.—The flask in which the sulphides are precipitated must be cleaned with chromic acid before use, to prevent adherence of the precipitate to the sides. If the solution analysed is originally acid, it is neutralised with soda until turbidity appears and this is just removed by adding a few drops of hydrochloric acid. The filtrate after the removal of the analytical sub-group IIIA from IIIB may be used for the separation (*cf.* Ostroumov, Abst., ANALYST, **1936**, **61**, 723, 795; **1937**, **62**, 495; **1938**, 214). If the volume is not too great the separation may be made after adding the pyridine salt and heating. Duplicate analyses of the mineral "asbolan" were in satisfactory agreement. The presence of pyridine in the solution of manganese chloride facilitates precipitation of the manganese ammonium phosphate. E. B. D.

Determination of Iron in the Presence of Titanium by the Jones Reductor Method. E. Truog and R. W. Pearson. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 631–632.)—In agreement with results of previous workers it was found that the interference by titanium in the oxidimetric titration method for iron involving the use of amalgamated zinc for reduction can easily be eliminated by aeration immediately after reduction in order to re-oxidise the titanium selectively. This selective oxidation by aeration after passage of the solution through the Jones reductor is now found to be better effected by adding distilled water containing dissolved air and stirring for a few minutes than by aspiration. The necessity for aeration is shown by the presence of the violet colour of tervalent titanium in the iron solution to be titrated. S. G. C.

***p*-Hydroxyphenylarsonic Acid as a Reagent for Titanium and Zirconium. C. T. Simpson and G. C. Chandlee.** (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 642–643.)—*p*-Hydroxyphenylarsonic acid has been found to separate titanium, by precipitation, from the following ions: ferric, ferrous, aluminium, zinc, cobalt, nickel, beryllium, chromic, manganous, calcium, magnesium, thallium, cerous, thorium, alkalis, phosphate, molybdate, chromate, vanadate, permanganate, uranyl and vanadyl. Interfering ions are zirconium, ceric and tin. Hydrogen peroxide interferes with the precipitation of titanium. The reagent may also be used to determine zirconium in the presence of the above-mentioned ions, and zirconium may be separated from titanium if hydrogen peroxide is present; ceric, tin, and phosphate ions, in more than very small amounts, interfere.

Titanium.—The solution (200 ml.) should contain not more than 0·06 g. of titanium oxide and the amount of acid present should be such that the solution will be approximately, but not more than, 0·6 *N* in hydrochloric acid or 1·8 *N* in sulphuric acid after the reagents have been added and precipitation is complete;

2 to 3 g. of ammonium thiocyanate are added if iron is present. The solution is heated to boiling and 100 ml. of 4 per cent. aqueous *p*-hydroxyphenylarsonic acid are added; the boiling is continued for 15 minutes to assist coagulation of the precipitate. After cooling, the precipitate is filtered off and washed first with 0·25 *N* hydrochloric or sulphuric acid containing about 0·5 g. of the reagent per 100 ml. (and about 1 per cent. of ammonium thiocyanate if iron is present), and finally with dilute (2 per cent.) ammonium nitrate solution; the precipitate is ignited and weighed as titanium dioxide. A fume-hood is required for the ignition, presumably to remove arsenic. An average deviation of 0·7 part per thousand was found in the results with pure titanium solutions. Among examples given of the applicability of the method, titanium was precipitated direct from solutions of a 2-g. sample of chrome-vanadium steel, a 5-g. sample of iron ore, 2-g. samples of an alumino-silicate refractory and a plastic clay; the results agreed well with those obtained by other processes..

Zirconium.—In the method outlined for titanium zirconium is also precipitated. The zirconium alone may be precipitated in the presence of excess of hydrogen peroxide, while in a second sample zirconium and titanium can be precipitated together (without addition of hydrogen peroxide) and determined as the mixed oxides. Alternatively, following precipitation of zirconium in the presence of hydrogen peroxide, the titanium may be determined in the filtrate after evaporation to "white fumes" with sulphuric acid in the presence of nitric acid to decompose complex titanium compounds. S. G. C.

Determination of Germanium in Minerals and Solutions. W. C. Aitkenhead and A. R. Middleton. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 633–635.)—*Minerals.*—To a 1-g. sample of the finely ground mineral contained in a platinum dish 10 ml. of nitric acid, 10 ml. of hydrofluoric acid and 2 ml. of sulphuric acid (1:1) are added, and the liquid is evaporated slowly, below the b.p. to avoid loss of germanium, until the hydrofluoric acid has been expelled (as judged by absence of white fumes when a strip of damp paper is held over the dish); the heating should not be sufficient to produce fumes of sulphuric acid. The contents of the dish are transferred to a beaker and made alkaline with sodium hydroxide; about 0·5 g. of sodium sulphide crystals are added, and the liquid is boiled for 15 minutes in order to dissolve any germanium oxide which may have separated during the slow acid-evaporation process. After cooling, the liquid is rendered just acid with sulphuric acid, and the precipitate of sulphur is filtered off after sufficient time has been allowed for it to coagulate. To the filtrate containing the germanium, as thiogermanate, 1·5 times its volume of conc. hydrochloric acid are added, together with 2 to 3 g. of finely divided precipitated copper, which serves to precipitate arsenic and antimony. If blackened within 1 hour owing to the presence of these elements, the copper must be filtered off and more added. *Distillation of Germanium.*—The liquid containing the copper is distilled in a flask fitted with a tap-funnel and a side-tube leading up to a vertical Liebig condenser; the upper end of the condenser is joined to one arm of a leading tube of inverted U-shape having a safety bulb blown in the other arm, the end of which dips into 5 ml. of water in an ice-cooled receiving tube. The distillation is continued until the water in the receiver becomes saturated with hydrogen chloride; if this fails to occur within about half-an-hour some conc. hydrochloric acid should be added to the distillation flask. *Determination by modified Marsh Test.*—This method should be used for small amounts of germanium (0·1 to 0·001 mg.). About 5 g. of pure zinc are placed in a 20-cm. test tube, to serve as generator, provided with a stopper carrying a dropping funnel and a delivery tube leading to a train consisting of a small wash bottle containing water, a drying tube loosely packed with glass wool, and a combustion tube of Pyrex glass, 12·5 cm. long × 0·6 cm. diameter, drawn out to a capillary, 5 cm. long and about 1 mm. internal diameter at the remote end. About 5 ml. of conc. hydrochloric acid are first run slowly into the generator and the combustion tube is heated, the usual precautions being observed. The germanium-containing distillate is then allowed to flow into the generator at about 1 drop per second, and finally a second 5-ml. quantity of conc. hydrochloric acid is similarly run in. The stain obtained is compared with standard stains made by operating with known amounts of germanium. The zinc used should preferably be in the form of flakes, and prepared by breaking up thin electro-deposited zinc sheet. *Gravimetric Determination.*—For amounts of germanium larger than can be dealt with by the Marsh method, the usual method of precipitation as germanium sulphide and conversion into germanium dioxide can be used. Alternatively, the distillate may be evaporated as follows:—An equal volume of 27 *N* hydrofluoric acid is added to the distillate contained in a platinum dish; 1 ml. of conc. sulphuric acid and 1 ml. of 60 per cent. perchloric acid are added, and the liquid is allowed to evaporate as far as possible on a steam-bath; the residue is then slowly evaporated to dryness by heating to a higher temperature, ignited and weighed as germanium dioxide. The application of these methods to the determination of germanium in solutions follows closely on that described above for treatment of a mineral which has been brought into solution. S. G. C.

Determination of Traces of Rhenium in Pyrolusite. L. C. Hurd and C. F. Hiskey. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 623–626.)—The amounts of rhenium considered were of the order of 1 p.p.m. or less. The sample of pyrolusite (100 g.) is dissolved in conc. hydrochloric acid with gentle heating. Any sandy residue is filtered off and extracted with boiling hydrochloric acid, the extract after filtration being added to the main solution and the residue rejected. Sufficient stannous chloride solution is added to reduce ferric and manganic chlorides to the bivalent state; 0·6 g. of potassium thiocyanate per 100 ml. together with a further 0·5 g. of stannous chloride per 100 ml. are added. Any rhenium or molybdenum present form a coloured thiocyanate, which is extracted by shaking with several successive portions of ethyl ether. After removal of the bulk of the ether by distillation from the combined extracts, 15 ml. of hydrochloric acid (sp.gr. 1·1) are added, and the remaining ether is removed in a current of air. The solution is oxidised with hydrogen peroxide, added, drop by drop, until no colour remains; the solution should be kept at this stage for 15 minutes and any colour which develops must be discharged with hydrogen peroxide. Separation of rhenium from molybdenum is effected by distillation of the liquid, diluted to 200 ml.

with conc. sulphuric acid, at 270° to 290° C. for 2 hours, in a slow stream of a mixture of steam and carbon dioxide, the distillate containing the rhenium being collected in an ice-cooled receiver. Bromine is added, to oxidise sulphur dioxide, until a faint yellow colour is produced; 100 ml. of conc. hydrochloric acid are added, followed, after cooling, by 10 ml. of 20 per cent. potassium thiocyanate solution and 15 ml. of 20 per cent. stannous chloride solution. The rhenium thiocyanate colour is matched against standards containing similar amounts of acid and reagents to which known amounts of rhenium (as perrhenate) have been added. The results in test experiments with traces of rhenium (0·2 to 2 p.p.m.) added to rhenium-free pyrolusite samples were reasonably good. Of 80 samples of pyrolusite from different parts of the world, the majority were found to contain no rhenium. The largest proportion found, in an ore from Montana, was 0·2 p.p.m.

S. G. C.

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Determination of Vanadium. A. F. Andreev. (*Zav. Lab.*, **1938**, **7**, 258–262.)—This is a modification of Someya's method of oxidising bivalent vanadium, using a reduced dyestuff as indicator (*cf. Z. anorg. Chem.*, **1924**, **138**, 291; **1928**, **169**, 293). Berry (ANALYST, **1934**, **59**, **736**) found that the oxidation was always too low (usually about 95 per cent. of theory) when phenosafranine was used as indicator and ferric alum as the oxidising agent, even when great care was taken to avoid oxidation of the vanadous salts by air. Also, the presence of molybdenum interferes with the reaction when any of the dyes mentioned by Someya are used as indicator. Acid fuchsin or trypan red, however, do not react with molybdenum. To obtain a satisfactory pink end-point with acid fuchsin the dye itself is used as the oxidising agent. For the reduction of vanadium to the bivalent state either zinc or cadmium may be used, preferably as amalgam. It was found that under the experimental conditions used chromium was reduced by zinc amalgam but not by cadmium; hence cadmium amalgam was used for further investigations. In the method of analysis worked out it is necessary to boil the reduced solution with acid fuchsin, otherwise the reaction is too slow. With trypan red, the titration can be carried out in the cold. This dye is therefore preferable, owing to the increased tendency of vanadous salts to become oxidised on heating. The reduction is effected in a conical flask provided with a ground-in stopper and having two glass tubes fused in on opposite sides; in each tube there is a glass tap. If about 50 ml. of the solution under examination are vigorously shaken with the amalgam the reduction, which must be made as usual in an air-free atmosphere, is complete in 20 minutes. The amalgam is then poured off through one tube while carbon dioxide is introduced through the other, and the titration is done immediately. The method is suitable for the determination of vanadium in steel, and the presence of titanium (as well as of chromium or molybdenum) does not interfere (except that when molybdenum is present the end-point is yellow, not pink), but tungsten must first be removed. *Determination in Steel.*—One g. of the sample is dissolved in 20 ml. of sulphuric acid (1:5) and 8 ml. of hydrofluoric acid (1:3), and oxidised by heating with a saturated solution of potassium permanganate. Excess of permanganate is removed with a few drops of hydrogen peroxide and the solution is transferred to a 250-ml. flask and made up to the mark with 4 *N* sulphuric acid. The determination is made on 50 ml. of the solution, as described above. If tungsten is present the steel solution is oxidised with nitric acid, added drop by drop, evaporated to fuming, diluted with water, again evaporated to fuming, filtered from the tungsten and made up to 250 ml. (The solution analysed must be completely free from nitric acid.) In test determinations on three steels of known composition the percentage results were:

	Found	Present
1 (tungsten present)	1·05; 1·07; 1·05	1·10
2 (tungsten absent)	0·26; 0·27	0·26
3 (tungsten absent)	0·70; 0·72	0·70

The water for the trypan red standard solution (0·4 g. dye : 1 litre of 2 *N* sulphuric acid) must be boiled for a long time to remove dissolved oxygen. The solution is standardised against reduced vanadium. Particulars of the preparation of the amalgam are given, and also results of preliminary experimental work. E. B. D.

Volumetric Determination of Vanadium in presence of Tungsten, with Diphenylamine-sulphonic Acid as Indicator. G. A. Pevtzov. (*Zav. Lab.*, 1938, 7, 286–289.)—For the determination of vanadium in the presence of tungsten it is essential to introduce sufficient phosphoric acid into the solution before the addition of the indicator and titration with ferrous ammonium sulphate solution. A large excess of the phosphoric acid is necessary, otherwise a complex compound with the tungstic and vanadic acids is formed; the vanadic acid complex is not decomposed on further addition of phosphoric acid and therefore not all the vanadium is titratable. Also, the yellow colour of this compound in solution reduces the sharpness of the end-point of the titration with diphenylamine sulphonic acid (with diphenylamine no definite end-point is obtained). The method used was that of Kolthoff and Sarver (*J. Amer. Chem. Soc.*, 1931, 53, 2906), but the solutions examined experimentally were more acid. Ten ml. of approximately *N*/100 vanadic acid solution, prepared from the pentoxide, were treated with *x* ml. of a 1 per cent. solution of sodium tungstate ($Na_2WO_42H_2O$), 10 ml. of a solution (either 25 or 85 per cent.) of phosphoric acid, 10-*x* ml. of water, 2 ml. of sulphuric acid (sp.gr. 1·84) and, finally, the indicator as the barium salt of diphenylaminesulphonic acid (*cf.* Kolthoff, *loc. cit.*). The solution was titrated with N/100 ferrous ammonium sulphate solution. With 25 per cent. phosphoric acid the results became lower as the concentration of tungsten rose, and with the ratio V:W = 1:5 the end-point was not sharp; addition of 85 per cent. phosphoric acid gave satisfactory results even with the ratio V:W=1:10. Substitution of sodium pyrophosphate solution for the phosphoric acid was unsatisfactory. The vanadium reduced by the ferrous salt was slowly re-oxidised, and this was not prevented by working in an atmosphere of carbon dioxide. Under the usual experimental conditions the amount of re-oxidation was insignificant (approximately 1 per cent.). E. B. D.

Utilisation of Raney's Alloy as a Substitute for Devarda's Alloy in the Determination of Nitrates. E. Cattelain and P. Chabrier. (*Ann. Chim. anal.*, 1938, 20, 285.)—Raney's alloy (nickel 30, aluminium 70 per cent.)

can be used instead of Devarda's alloy (copper 50, aluminium 45, zinc 5 per cent.) in the determination of nitrates by reduction to ammonia in an alkaline medium. The technique has been described previously (Cattelain, *J. Phys. Chim.*, 1934, **20**, 118). The results obtained in test experiments with potassium nitrate agreed closely with the theoretical values. E. M. P.

Determination of Dissolved Oxygen in Condensed Steam. J. Haslam and G. Moses. (*J. Soc. Chem. Ind.*, 1938, **57**, 344–347T.)—The method of McCrumb and Kenny (*J. Amer. Waterworks Assoc.*, 1929, **21**, 400) has been modified so as to eliminate errors arising from contamination of the reagents and permanent colour standards during preparation and storage, and from contamination of alkaline suspensions of manganous hydroxide by atmospheric oxygen. The method depends on the oxidation of manganous hydroxide by the dissolved oxygen, followed by solution of the oxidised manganese compounds in dilute hydrochloric acid, and application of the *o*-tolidine colour reaction. The (B.D.H.) *o*-tolidine was purified by heating 10 g. in a Carius tube at 160° to 180° C. for 7 hours with 50 ml. of acetic anhydride, the pressure being released on the following day, and the contents of the tube poured out in the molten state after the necessary period of immersion in a boiling water-bath. The liquid was then cooled in ice, and the tetra-acetyl derivative was filtered off on a sintered glass crucible (17G3) with suction and dissolved in the minimum amount of boiling water, and distilled water was added to the solution until a slight permanent turbidity was produced. The mixture was boiled under a reflux condenser with 2 g. of animal charcoal for 2 hours and filtered in a funnel having a hot-water jacket, and the crystals were separated from the cool filtrate by filtration and washed with dilute alcohol. Ice was added to the mother-liquor until its volume had increased 3-fold, and the precipitated crystals were again separated by filtration, washed, and finally dried at 100° C. They were then hydrolysed by boiling 2 g. for 5 to 6 hours under a reflux condenser with 50 ml. of conc. hydrochloric acid and 10 ml. of water. Water was added to the cool mixture to dissolve any precipitated crystals, and the liquid was filtered and made alkaline with 10 per cent. sodium hydroxide solution. The precipitated crystals of *o*-tolidine were finally separated by filtration, washed well with water and recrystallised from dilute alcohol; m.p. 129° C. (uncorr.). Lea's conclusion, that purified *o*-tolidine has an increased sensitiveness, was confirmed (*cf. J. Soc. Chem. Ind.*, 1933, **52**, 245T), but the product obtained by his method of purification appeared to be the diacetyl derivative. A method and apparatus for the production of water free from dissolved oxygen is described in which a stream of nitrogen is passed for 20 to 24 hours, first through 2 wash-bottles in series containing an alkaline solution of pyrogallol, then through another pair of wash-bottles containing water, and finally through a sintered glass disc in the bottom of an aspirator containing 10 litres of the water to be purified. The solutions were stored in an atmosphere of nitrogen, and an apparatus for this purpose and for treating the water is shown in a diagram. Ordinary distilled water saturated with air was used as a reference water of known oxygen-content, the dissolved oxygen being determined by a modification of Winkler's method. A special sampling bottle is also illustrated; a feature of it is the sunken stopper, one side of which has a projecting portion which, when opposite a corresponding depression in the neck of the bottle, leaves a small space between the stopper and the neck, or when twisted so that the projecting portion is on the other (*i.e.* straight) side of the neck, effects a complete closure of the bottle. The bottle was filled with the purified water, a measured volume of the water of known dissolved oxygen-content was then added rapidly, followed by 0·25 ml. each of a 40 per cent. solution of manganous chloride ($MnCl_2,4H_2O$) and a 70 per cent. solution of potassium hydroxide in the purified water in both instances. These additions were made at the bottom of the bottle by means of special delivery burettes, so that the water near the top of the bottle, which had come into contact with the air, was ejected. The stoppered bottle was then inverted gently 3 times, and 1 ml. of conc. hydrochloric acid (which was stored in the dark) was introduced through the special stopper (see above), so that the contents of the bottle were not exposed to the air even momentarily. When the hydroxides had completely dissolved, 1 ml. of a solution of 1 g. of *o*-tolidine in 10 ml. of the hydrochloric acid, diluted to 100 ml., was added, and after exactly 5 minutes the resulting colour was matched against permanent colour standards prepared (after Yoe, *Photometric Chemical Analysis*, Vol. I, p. 157) from mixtures of solutions containing (*a*) 3·75 g. of copper sulphate and 2·5 ml. of conc. sulphuric acid in 250 ml.; (*b*) 0·625 g. of potassium dichromate and 2·5 ml. of the acid in 250 ml. The volumes (in ml.) of (*a*) and (*b*), which must be mixed and diluted to 100 ml., and the dissolved oxygen contents (in ml. per litre), to which they are then equivalent in colour, respectively, are:—0·05, 0, 0·001; 0·34, 0, 0·005; 0·69, 0·95, 0·01; 1·90, 1·89, 0·05 and 3·14, 1·92, 0·05. The method was tested with waters of known dissolved oxygen-contents (0 to 0·048 ml. per litre), and the maximum error was 0·008 ml. per litre. An apparatus for sampling condensed steam without contamination from the atmosphere is described, in which the condenser main is tapped through a valve by a sampling-tube and the steam is condensed in a block-tin cooling tube, whence the sample flows into the special sampling-bottle; the whole apparatus is flushed out well with the sample beforehand. Six determinations on each of 8 samples are recorded; the mean values varied between 0·011 and 0·016 ml. per litre, and the agreement between the duplicates was satisfactory. The absence of other substances which might affect the colour produced with the reagent should be established by measuring the effects of the addition of known quantities of water of known dissolved oxygen-content. J. G.

Microchemical

Method for the Estimation of Ultramicro-quantities of Lactic Acid. B. F. Miller and J. A. Muntz. (*J. Biol. Chem.*, 1938, **126**, 413–421.)—A method whereby as little as 0·1γ of lactic acid can be estimated was devised for use in the investigation of dental caries. The method was based on the highly sensitive colour reaction of Eegriwe (*Z. anal. Chem.*, 1933, **95**, 323). Lactic acid is oxidised to acetaldehyde by hot conc. sulphuric acid, and the acetaldehyde produces an intense bluish-violet colour with *p*-hydroxydiphenyl. Exactly 0·2 ml. of the sample is measured into a glass-stoppered Pyrex test-tube, which is immersed in ice-water while 1·5 ml. of conc. sulphuric acid is added slowly. The tube is then stoppered, the ground-glass portion being lubricated with a drop of the acid, and the contents are gently shaken. The tube is heated in a boiling water-bath for 5 minutes and then cooled in ice-water for 10 to 15 minutes. Eight mg. (±0·2 mg.) of very finely powdered *p*-hydroxydiphenyl (purified by repeated crystallisation from cold acetone solution) are then carefully added through a funnel to avoid scattering the powder on the side of the tube. The tube is re-stoppered and the contents are gently but thoroughly mixed, care being taken to avoid splashing the walls of the tube. The maximum colour development is obtained by allowing the tube to stand for an hour at room temperature, after which it is immersed in a boiling water-bath for exactly 90 seconds and cooled immediately. The colour of the solution is measured with a Pulfrich photometer with S57 filter. The value of the extinction coefficient thus obtained is converted to γ of lactic acid per 0·2 ml. of the sample by means of a calibration chart. Teeth or carious matter are pulverised and extracted with water, and an aliquot portion of the solution is treated as described above. Blood serum is treated with an equal volume of a freshly made 7 per cent. solution of metaphosphoric acid and 8 volumes of water. After being thoroughly shaken and left for 10 minutes the solution is centrifuged and an aliquot portion of the supernatant liquid is taken for analysis. Saliva is merely diluted with an equal volume of water. The reaction is remarkably specific; pyruvic acid gives a colour under the conditions outlined above, but its interference can be eliminated by prolonging the oxidation with sulphuric acid to 15 minutes. Other acids and carbohydrates do not interfere at all. Analyses made with pure lithium lactate gave duplicate results varying by 2 to 3 per cent. with quantities of 3 to 10γ. F. A. R.

Catalytic Colour Reaction for Tungsten. E. B. Sandell. (*Ind. Eng. Chem., Anal Ed.*, 1938, 10, 667–668.)—Sexivalent tungsten markedly catalyses the reaction between titanous chloride and malachite green, which normally proceeds very slowly at room temperature, the tungsten becoming rapidly reduced by titanous chloride, giving reduction products that reduce malachite green to the leuco form. The reaction may be applied in detecting tungsten as follows:—To a 0·05-ml. drop of the solution (which may be neutral or 0·1 *N* in hydrochloric acid), placed on a spot plate, is added 0·01 ml. of 1 per cent. titanous chloride solution followed by 0·01 ml. of a 0·005 per cent. aqueous malachite green solution. With 10 p.p.m. of tungsten in neutral solution the blue-green colour fades in about 3 seconds; with 2 p.p.m. it is decolorised in 1 to 1·5 minutes, and with 1 p.p.m. in 3 minutes. In absence of tungsten the drop remains coloured for 4 to 5 minutes. The limit of sensitiveness is considered to be 2 p.p.m. When the test-drop is 0·1 *N* in hydrochloric acid, the reaction with tungsten is a little slower; the smallest amount detectable is 4 p.p.m., the fading occurring in 2 to 3 minutes, whilst the drop remains coloured for 3·5 to 4 minutes in absence of tungsten. The reaction fails, owing to consumption of the titanous chloride, when appreciable amounts of reducible salts are present, such as those of iron, uranium and vanadium in the higher valency state, or cations which are reduced to metal or form insoluble chlorides. Other interfering substances are: sulphate, nitrate, tartrate, phosphate and fluoride. Molybdenum catalyses the reaction between titanous chloride and malachite green, but its effect is much less than that of tungsten. S. G. C.

Micro-determination of Magnesium in pure Solutions and in Blood Serum. M. Delaville and M. Olive. (*Ann. Chim. anal.*, 1938; **20**, 286–287.)—The authors recommend a modification of Berg's 8-hydroxyquinoline method, in which the metallic ion is determined instead of the hydroxyquinoline. In testing the method the following procedure was adopted:—A known volume of magnesium sulphate solution was neutralised with *N* sodium hydroxide solution, neutral red being used as an indicator, and 1 ml. of the sodium hydroxide solution was added in excess. The liquid was treated with 1 ml. of a saturated solution of sodium potassium tartrate and finally with 0·3 to 0·4 ml. of a 5 per cent. alcoholic solution of 8-hydroxyquinoline. The mixture was heated on a boiling water-bath for 4 to 5 minutes and centrifuged, and the supernatant liquid was decanted. The precipitate was washed with water, with centrifuging after each washing, until the washings were neutral. Two or four ml. of *N*/40 hydrochloric acid were added, the liquid was warmed on a water-bath until the precipitate had dissolved completely, and the acid was titrated hot with *N*/100 sodium hydroxide solution, in the presence of neutral red. The results obtained are shown in a table. The results obtained with quantities of magnesium sulphate ranging from 0·6 to 0·012 mg. agreed with theory within ±3 per cent.

The following procedure is used for the analysis of blood serum:—Two ml. of serum are evaporated to dryness in a platinum crucible on the water-bath, and the residue is ignited to give a white ash, which is taken up in a mixture of 2 ml. of conc. hydrochloric acid and 2 ml. of water, and then treated with 1 ml. of a solution of 6·40 g. of oxalic acid in 100 ml. of *N* hydrochloric acid made up to 1 litre with water. The crucible is covered with a watch-glass and heated for 30 minutes on the water-bath. The liquid is treated with 2 ml. of saturated ammonium oxalate solution, cooled, made alkaline to phenolphthalein (1 drop) with ammonia, and left for 2 hours. The precipitate is filtered off and washed with a little ammonium oxalate solution, the washings being combined with the filtrate. The residue on the filter-paper is calcium oxalate and can be determined if the calcium-content is required. The filtrate is evaporated to dryness and the crucible is heated carefully over a Bunsen burner to decompose the ammonium salts. The residue is taken up in 1 ml. of conc. hydrochloric acid and warmed on the water-bath until the ash has completely dissolved. The liquid is transferred to a centrifuge tube, and the determination is completed as above, care being taken to neutralise the acid completely. When 2 ml. of *N*/40 hydrochloric acid are used, the results are calculated from the formula

$$\text{magnesium, in mg.} = (5 - N) \times 0{\cdot}12,$$

where *N* is the number of ml. of *N*/100 sodium hydroxide solution used in the titration. The centrifuging can be carried out more easily by adding 1 ml. of 95 per cent. alcohol, which prevents the precipitate from creeping up the sides of the tube. E. M. P.

Reviews

(1) Organic and Bio-chemistry. By R. H. A. Plimmer, D.Sc. 6th Edition. Pp. x + 623, with coloured plate and illustrations in text. London: Longmans, Green & Co. 1938. Price 21s.

(2) A Textbook of Biochemistry. By Roger J. Williams, Ph.D., D.Sc. Pp. x + 525. London: Chapman & Hall, Ltd. 1938. Price 21s.

(3) Outlines of Biochemistry. The Organic Chemistry and the Physico-chemical Reactions of Biologically Important Compounds and Systems. By Ross Aiken Gortner. 2nd Edition. Pp. xx + 1017. London: Chapman & Hall, Ltd.; New York: John Wiley & Sons, Inc. 1938. Price 30s.

(1) Text-books of biochemistry must now constitute almost one of the principal exports from the United States of America to this country. "Plimmer" has the burdensome responsibility of being the senior representative of indigenous works covering the rapidly widening ground in this flourishing branch of chemical science. First published in September, 1910, as *Practical Physiological Chemistry*, it has passed through six editions or impressions; the new edition is separated by five years from the last.

Professor Plimmer's book differs from most of the others in being largely, though by no means exclusively, a practical hand-book for student and research worker in the laboratory. In the second edition (1915) the title was changed to *Practical Organic and Bio-chemistry*; in the fourth edition (1926) the theoretical part was considerably enlarged, so that it became an admirable introduction to organic chemistry for the medical student or biological worker, and the word "practical" was omitted from the title.

Nevertheless, it is as a practical guide to reactions and preparations—especially the isolation of pure substances from natural sources—that it stands in a unique position, and can well hold its own against American competitors. The new edition brings up to date many of those biochemical subjects that have been the recent object of intensive study. Thus mention is made of the anti-pellagral action of nicotinic acid; a short chapter is devoted to the composition of the nucleic acids; the modern formulation of sterols, sex hormones and anti-rachitic vitamins is clearly presented; the chapter on pigments includes descriptions of anthoxanthins, anthocyanins, haemin and the porphyrins, chlorophyll and the carotenoids or lipochromes. If one were to suggest any additions to a book in the writing of which the problem of compression must be most difficult, it might be more emphasis on the presence of *d*-ribose in many physiologically important substances, especially in association with phosphoric acid; a brief reference to one of the most important (and mysterious) properties of proteins, their "specific dynamic action"; and some slight account of the fascinating connection now established between certain water-soluble vitamins and co-enzymes. Emphasis might also be laid on the "mixed" nature of the glycerides in many fats and oils.

The volume is admirably produced, and concludes with some useful tables, a list of reagents (including indicators) and a full index. Random sampling has failed to reveal any typographical errors. Professor Plimmer's book has achieved the classical status that results from an excellence witnessed by 28 years' existence and five re-editings. Long may he continue to be both able and willing to keep his work as up-to-date and authoritative as on this occasion.

(2) Professor Williams has written a companion to his earlier *An Introduction to Biochemistry* (1921). There the emphasis was on the vegetable kingdom; here he is concerned mainly with the animal, and especially with man. After Part I, which is called *Biochemical Materials* and discusses the chemistry of both inorganic and organic constituents of the living body, the book is mainly devoted to consideration of the physical and chemical reactions in which those substances take part. Although the amount of information to be found in these 500 pages is most extensive, it is presented in a fluent and persuasive manner. The work can almost be recommended as a "bed-book," for it can be picked up and read with profit and interest wherever it happens to be opened.

(3) Professor Gortner has set himself a task rather different from that of most writers of biochemical books. Without in any way overlooking the practice and methods of the science, he is chiefly concerned with the nature of the phenomena investigated. He is not afraid to speculate, when speculation is called for; indeed he has apparently been so much interested in this approach as to have failed to note certain rather unfortunate slips in the presentation of the facts (witness "2.2-dihydroergosterol" instead of "22-dihydroergosterol," and "irridation" for "irradiation," both on p. 895). Co-enzymes, though discussed in the text, receive no mention in the index, which is full, occupying 61 pages—23 for authors and 38 for subjects.

The scope of the book is most impressive. The author must indeed be an enthusiast for his subject, particularly for the more philosophical aspects thereof, and it can be confidently recommended to those who have perhaps a rather *recherché* taste for the interrelations of chemical substances in the living organism.

A. L. BACHARACH

AN INTRODUCTION TO INDUSTRIAL MYCOLOGY. By GEORGE SMITH, M.Sc., A.I.C. Pp. xii + 302 + 64 plates. London: Edward Arnold & Co. 1938. Price 16s. net.

This book might be described as a text-book on the mycology of the fungi with special reference to those of importance in industry. It is introductory in so far that it does not presume upon a knowledge of mycology by the reader, all terms, methods of identification, systems of classification, methods of manipulation, and so forth, being sufficiently explained; on the other hand, it is more than elementary, for a very large number of genera and species are described, those of greatest importance and most common occurrence being considered in proportionate detail.

The book opens with a foreword by Professor Raistrick of the London School of Hygiene and Tropical Medicine, at which school the author is research demonstrator, and then comes the author's preface. The first chapters are introductory. Terminology and principles of classification are dealt with and well illustrated;

the author has adopted the same system of classification as Rabenhorst in his *Kryptogamenflora*, in which the *Eumycetes* are divided into two main groups: *Phycomycetes* and *Mycomycetes*, and these into five classes: *Oomycetes*, *Lygomycetes*, *Ascomycetes*, *Basidiomycetes* and *Fungi Imperfecti*. The following six chapters are devoted to the subdivision of these classes into orders, families and genera, the distinguishing characters of which are well described and most beautifully illustrated by 256 excellent original photomicrographs, the magnifications of which are specified. Thus the order of the *Hyphomycetales* of the *Fungi Imperfecti* is divided into four families, of which the *Mucedinaceae* is one; a key of the subdivision of the *Mucedinaceae* into 11 more important genera is given and the text proceeds to the description of these genera. Here the reviewer has one slight criticism to offer: there is not quite sufficient contrast between the type of the headings to the genera and the orders. On page 86, for instance, it would help the reader if the heading of the order *Dematiaceae* stood out in rather stronger contrast with the heading of the genus *Tricothecium*. While generally a paragraph is devoted to the description of each genus, a chapter each is given to the description of the genus *Aspergillus* and to the genus and related genera *Penicillium*, 12 species of the former and 40 to 50 of the latter being described. These chapters are very well written; while easy to read, they are not in any way lacking in essential detail.

Then follows a chapter on laboratory equipment and technique, including the preparation of culture media and methods of making and examining cultures, methods of isolating moulds and making pure cultures, microscopic equipment, and methods of identification of species—a useful outline of the procedures necessary. This chapter contains many useful hints, such as the benefit to be derived from the use of the 8-mm. objective instead of the 4 mm. (or 1/6th), and of the 3-mm. oil immersion instead of the 2-mm., the loss of magnification being compensated by the use of a higher-power ocular. If by this means the author was enabled to obtain the superb photomicrographs reproduced in Figures 74 and 98, giving a magnification of 1000 diameters and an almost perfectly flat field, this suggestion does not need a stronger recommendation.

The next three chapters deal with the physiology of mould fungi: Chapter X with food requirement, respiration, reaction of medium, influence of light, temperature relationships, moisture requirements, poisons, influence of other fungi; Chapter XI with the maintenance of culture collections; Chapter XII with the control of mould growth in factory and industrial conditions.

Chapter XIII gives a brief account of the industrial uses of fungi, under the following headings:—Alcoholic Fermentation and Mould Enzymes, Mould-ripened Cheese, Oxalic and Citric Acids, Gluconic Acid, Gallic Acid, Fats, Proteins, Vitamins and Miscellaneous Products of Moulds and Fungi and the Soil. Chapter XIV, headed "Mycological Literature," gives a list of publications to which the reader is referred for a more specialised account of fungi than comes within the scope of the present work; these publications, of which a brief but very useful summary is given, include general works, monographs, books on general and systematic mycology and applied mycology, journals and periodicals.

This book should be of the greatest value to works' chemists faced with the problem of mould contamination, as for instance in margarine works, and with its aid it should not be difficult to identify the species, or at least the genus, concerned, and to devise suitable measures for its suppression.

The book is well printed, the type is very readable, the paper is good, and there is a good index; the outstanding feature is the excellence and the very liberal number of the plates. The author, publishers and printers deserve warm praise for the production of the work, which must have involved a large amount of labour, and it can be confidently recommended not only to those who wish to acquire a first-hand and at the same time quite considerable knowledge of the mould fungi, but to all who desire a concise hand-book on the subject, suitable for ready reference.

D. R. WOOD

CHEMISCHE SPEKTRALANALYSE. By W. SEITH and K. RUTHARDT. Pp. vi + 103, 60 illustrations and 2 plates. Berlin: Julius Springer. 1938. Price RM.7.50.

In recent years the use of spectrochemical methods for quantitative estimations of elements and certain classes of compounds has become more widespread in chemical laboratories. A striking example of its use is the detection and estimation of small proportions of strontium in a calcium salt prepared for re-determination of the atomic weight. Gerlach determined the proportions of strontium, and thus was able to supply the necessary corrections. The rapidity and convenience of the method are now appreciated, but there are few books available for the chemist who desires information as to the best methods of procedure. Messrs. A. Hilger, Ltd., have issued translations of Gerlach's and his colleagues' monographs, and also some informative booklets on the use of spectrographic and spectroscopic methods, resulting from the work of Twyman and his co-workers. These are, of course, excellent in their own field, but, apart from Swings' small work issued in 1935, little of recent date is available to the chemist who desires to consult an introductory statement on the theory and application of the methods of spectral analysis.

The small volume, now to hand, fills a gap in this respect. It is a methods book and sets out the details clearly and sufficiently fully to enable the instructions to be followed intelligently. There are many practical examples, and these will be found useful as a guide in the first instance to those contemplating the use of the method. In the small compass of the book the subject can hardly be expected to be treated exhaustively, but success should follow strict adherence to the details given.

A general introductory chapter is devoted to sources of radiation and a short description of some Continental spectrographic apparatus, and a few pages to the elementary theory of the emission of spectrum lines. Fairly full instructions for arc and spark excitation are given and a discussion of the proper method of alignment of apparatus—a most important feature in spectrographic work—is furnished (pp. 27 *et seq.*). The section on qualitative analysis considers the question of purity of substances, and identification of lines of emission.

In the discussion of quantitative methods, "homologous pairs" as developed by Gerlach and Schweitzer is one of the recommended procedures. This method depends upon the selection of pairs of lines of an element which maintain their relative intensities on the photographic plates despite large variations in the conditions of excitation. If lines of this kind are found it will go far towards eliminating inaccuracies from small alterations in inductances and sparking potentials and photographic errors.

Visual examination of emission lines is also discussed, and examples refer to Ni, Mn and Cr in ferrous alloys, and also to cadmium in lead. The sparking of solutions of electrolytes is considered briefly, as is the production of high frequency sparks by the method of Walther Gerlach and Werner Gerlach. A few pages are devoted to absorption spectra of solutions, and there are two well-produced plates of the spectra of some of the commoner elements met with in spectrographic work. So far as this little volume goes, it is a good practical statement of the method and is free from errors. The beginner can safely follow the instructions; he will also be made to realise the need for careful calibration in special cases. Presumably, lack of space accounts for the absence of many references to the British, American, French and Belgian work on the subject and of Lundegårdh's outstanding contribution of the hot flame method.

J. J. FOX

A TREATISE ON LIGHT. By R. A. HOUSTON, M.A., D.Sc. 7th Edition. Pp. xi + 528, 2 coloured plates, 8 half-tone plates and 345 diagrams. London: Longmans, Green & Co. 1938. Price 14s.

This well-known text-book now appears in the seventh revised edition, and new matter is added. For the first time answers to the problems are given, and this is a definite advantage for the student working through the book systematically. The first quarter of the work deals with geometrical optics and includes optical methods and brief accounts of optical instruments. In the second part, dealing with physical optics, the chapters on polarisation, optical rotation and analysis of polarised light will interest chemists most. In the reviewer's opinion, these chapters contain such elements of the subject as should be known to those who employ instruments depending upon the use of polarised light. Magnetic rotation of the plane of polarisation and the Kerr effect receive rather scanty treatment.

The third part deals with spectroscopy and photometry. A good account of the simpler apparatus for use in the ultra-violet, visible and infra-red regions is furnished, together with some descriptions of gratings of various kinds. The account of X-rays and their application is extended a little and a very short statement on photoelectric cells is added. The chapter on the quantum theory is an elementary statement which does not go very far, but not much more can be expected in eighteen pages. The subjects of photometry and illumination are treated rather shortly, but the section on colour and colour vision, within its scope, is well set out, as would be expected from the author's authority on this subject.

For those who desire to obtain a fuller view of the mathematical theory of optics Part IV can be recommended. It requires some concentration to read this section, but with a little perseverance the subject matter is not too difficult to follow. The book was written for those who "are proceeding further with the study of light," and it has clearly fulfilled this objective, since it is now once again in a new edition.

The only serious criticism which can be brought is that some of the subjects, *e.g.* Raman spectra, receive very little attention. Nevertheless, the new edition, like the earlier ones, is an excellent treatise, with the advantage for chemists that the subject matter is presented so that it can, in the main, be grasped readily, with not too heavy a demand on mathematical equipment. Its form and bold print make it a pleasure to handle the book.

J. J. Fox

A TREATISE ON QUANTITATIVE INORGANIC ANALYSIS. WITH SPECIAL REFERENCE TO THE ANALYSIS OF CLAYS, SILICATES AND RELATED MINERALS. By J. W. MELLOR and H. V. THOMPSON. 2nd Edition. Pp. xxxi + 784. London: Charles Griffin & Co. 1938. Price 42s.

The first edition of this book has been out of print for the last ten years and unobtainable on loan from the principal chemical libraries or by purchase second-hand for the last five. The condition of such copies [illegible]re available in reference libraries speaks eloquently of the hard use to wh[illegible]y have been put. It is no exaggeration to say, therefore, that this second [illegible]on is overdue.

The reviewer is of opinion that the reason for the success of the first edition was not its special bearing on the ceramic industry, but the comprehensive nature of the contents, clarity of exposition and extreme lucidity of style combined with the critical ability and practical outlook of the author. That it should have been written by one whose life's work was closely connected with ceramics is due to the fortunate accident that the demands of that industry upon analytical chemistry cover some part of the requirements of almost all others. There can be but few problems of determination or separation of inorganic ions upon which some assistance or a new light cannot be obtained from "Mellor"; combined, in most instances, with some pleasure in the search, for he seems to have been a firm believer in gilding the philosophic pill.

It might be well if anyone handling this book for the first time would treat it as a general work on inorganic analysis, and disregarding the special emphasis on ceramics in sub-title and chapter headings, look up some troublesome separation or disputed point in a determination. He will probably be surprised at the amount of information to be obtained, either from the text itself or the very full footnotes and references that appear on every page.

Some of the old text has been revised and re-written where necessary; but much of the original writing has stood the test of time, and has every appearance of continuing to do so. Revision has consisted, for the most part, in removing the obsolete and incorporating selected methods discovered during the last twenty-five years, but only to such an extent as is, according to the author, justified by practical experience, and not with any idea of flying from the ills we have to "others that we know not of."

The printing is in the usual clear type, on the high quality paper and in the pleasing format that distinguish the productions of Messrs. Charles Griffin & Co. Another, less pleasing characteristic, is that the pages are fastened into the familiar brown cover in an inadequate fashion; the book may be expected to join ultimately the ranks of valuable broken-backed volumes on every chemist's book-shelf.

As the book has been for so long out of print, some indication of the nature of its contents would appear to be desirable. Part I (pp. 127) consists of an introductory essay on the history, scope and limitations of analytical chemistry, followed by a description of analytical procedure in general. This is written in the concise style and from the critical attitude adopted by the late Dr. Mellor in all his written work, and sets the general tone and outlook of the whole book; it is worthy of the attention of all practising and prospective analytical chemists.

The articles on sampling and preparation of the sample for analysis cover ground that is all too often unexplored, not only by chemists, but also by those in charge of the business side of operations that depend for their ultimate success on the laboratory valuation of raw materials and commercial products.

It is to be regretted that the opportunity has not been taken, while the type was being re-set, to revise the section on volumetric glassware and bring the text and correction tables for temperature into accordance with the new standard temperature for volumetric glassware (1934). The neglect of this piece of mechanical labour gives the book an out-of-date appearance that is quite at variance with the remainder of its contents. The directions for calibration of volumetric glassware also require revision to bring them into line with modern practice and N.P.L. requirements.

Part II (pp. 123) deals with the constituents of a typical silicate, including the alkalis. The respective merits and failings of the methods used for "opening up" are described in exhaustive detail, followed by articles on the separation of group precipitates and methods for the determination of the separate elements that would apply with equal force whatever their origin, and that are not specially distinctive of, or solely applicable to, silicates or ceramic materials. This is typical of the treatment throughout the whole book. Its usefulness does not cease with the disposal of the special problems created by the presence of silica. Especially noteworthy chapters are those on the ammonia precipitate and its sequelae, the determinations of iron, titanium, aluminium and beryllium.

Part III (pp. 171) treats of the separation and determination of arsenic, antimony, tin, lead, bismuth, mercury, copper, cadmium, zinc, manganese, cobalt, and nickel. Attention may be drawn to the section dealing with the behaviour of these elements in silica separations, and the essays on the theory and practice of separations by hydrogen sulphide.

Part IV (pp. 175) deals with molybdenum, tungsten, niobium, tantalum, gold, platinum, selenium, aluminium, beryllium, iron (special methods), chromium, vanadium, uranium, zirconium, thorium, part of the rare earth series, barium, strontium, calcium, magnesium, and lithium. Full use has been made of the work of Schoeller and his collaborators, whose methods have replaced the methods of Marignac and E. S. Simpson described in the first edition.

Part V (pp. 158) covers methods for the determination of free and combined carbon, water, boron, phosphorus, sulphur, and the halogens. It has been largely re-written, and contains some pertinent thoughts on the precautions necessary in weighing absorption tubes and on the properties of barium sulphate. The final chapter of this part consists of a description of methods used for the separation of mineral species in clays, the so-called "rational analysis," and a discussion on its value and place in the appraisal of argillaceous material. It is of interest to the specialist only.

Although by page numbering, this edition contains but six pages more than its predecessor, the actual number of new pages amounts to rather more than a hundred; the extra space for text has been obtained by removing 84 pages of appendix, the name index, many old blocks and some schematic diagrams.

The reviewer owes to the late Sir Herbert Jackson his introduction to the first edition of this work, which was accompanied by words to the effect that it was one of the best books on inorganic analysis ever written. During the past twenty-five years he has had many opportunities of confirming that opinion, and considers that it still holds true for this, the second edition.

The book contains a grateful and graceful tribute from Sir Robert Robertson to the memory of Dr. Mellor and his work. F. L. OKELL

FIELD DETERMINATION OF ROCKS. By E. H. DAVISON, B.Sc. Pp. vii + 87. London: Chapman & Hall. 1938. Price 7s. 6d. net.

The aim of this book is to assist geologists in the identification of rocks in the field; the classification of rocks is therefore based on such characters as texture, mode of occurrence and mineral composition. Rock-forming minerals are listed with such of their properties as can be determined in the field, and the texture, colour, mineral composition, mode of occurrence and field relations of rocks are discussed in some detail. Rock types are illustrated by a number of plates, and three useful tables show the method of classification. Although the classification is by no means ideal, it should prove of practical value to the field geologist, and the book should form a useful companion volume to the author's publication, *Field Tests for Minerals.* A. SHAW

LABORATORY MANUAL OF PHYSIOLOGICAL CHEMISTRY. MEYER BODANSKY and MARION FAY. Fourth Edition. Pp. vii + 295. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 10s.

The fourth edition of this excellent handbook does not differ materially from the third, which was reviewed in these pages three years ago (ANALYST, 1936, **61**, 75). Such changes as there are have been made ". . . in an attempt to clarify directions and to render them more workable for the elementary student." The book is essentially a manual for students, and its aim is declared to be ". . . to provide some experiments that were essentially of descriptive value and others which would acquaint the student with the quantitative procedures commonly employed in the analysis of urine, blood and other body fluids." It is incidentally, however, a useful book of reference for those analysts and research workers who may occasionally be required to determine the amounts of certain substances in biological material or to attempt their isolation. The book has disadvantages for this purpose, since assisting analysts and research workers is not its primary purpose, but it is nevertheless a useful little book to have available. For initiating students into the mysteries of biochemistry, and particularly of the biochemistry relating to the animal organism, it can be warmly recommended.

F. A. ROBINSON

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

ANALYTICAL METHODS COMMITTEE

SUB-COMMITTEE ON DETERMINATION OF UNPOLYMERISABLE MATTER IN OILS, WITH ESPECIAL REFERENCE TO TUNG OIL

A SUB-COMMITTEE has been appointed to consider the standardisation of a method for the Determination of Unpolymerisable Matter in Oils, with especial reference to Tung Oil. The Sub-Committee consists of Professor T. P. Hilditch, D.Sc., F.I.C. (Chairman), and Messrs. E. R. Bolton, F.I.C., M.I.Chem.E., G. T. Bray, A.I.C. (Hon. Sec.), H. E. Cox, D.Sc., F.I.C., B. A. Ellis, M.A., F.I.C., F. A. Hatch, F.I.C., and L. A. Jordan, D.Sc., F.I.C.

Deaths

WITH deep regret we record the deaths of

Mr. E. R. Bolton, Past President.
Dr. J. T. Dunn, Past President.
Mr. A. W. Knapp, former Member of Council.
Mr. H. Silvester, former Member of Council.
Professor A. Smithells, Honorary Member.

Obituary notices will be published later.

A New Method for Determining Hydrogen by Absorption in Technical Gas Analysis

BY H. N. BANERJEA, L. A. BHATT AND R. B. FORSTER, D.Sc., F.I.C.

THE determination of hydrogen in technical gas analysis presents considerable difficulty, especially when made by the fractional combustion method. In the analysis of the gases obtained by the carbonisation of Nepal lignite, concordant results could not be obtained for the hydrogen and saturated hydrocarbons. The fractional combustion was carried out in a modified Lunge–Orsat apparatus containing a fifth pipette which was connected to the manifold by a capillary containing palladised asbestos for the preferential combustion of the hydrogen. The variations in the results were presumably due to partial combustion of the hydrocarbons along with the combustion of the hydrogen in the presence of excess of oxygen.

As other workers[1] have experienced similar difficulties in this connection it was considered advisable that the hydrogen should be determined by an absorption method prior to the determination of the hydrocarbons in the explosion pipette.

Selective absorption of hydrogen in gas analysis has attracted attention for a considerable time. Campbell and Hart[2] proposed the use of a freshly-prepared nearly neutral 1 per cent. solution of palladous chloride for estimating small quantities of hydrogen. They found, however, that the absorption was very slow and that no advantage was gained by the use of acidic or more concentrated solutions. Bone and Jerdan[3] used oxidised palladium sponge to absorb hydrogen from mixtures of hydrogen and saturated hydrocarbons without affecting the latter, and Grice and Payman[4] applied this method to the determination of hydrogen in gas analysis.

Paal and Hartmann[5] used a solution of colloidal palladium and sodium picrate, but found that the absorption of hydrogen was very slow. Hempel[6] repeated the work of Paal and Hartmann, and found that the solution foamed badly and gradually lost its activity even in the absence of light. He tried the addition of a small quantity of alcohol to eliminate the foam, but found that it poisoned the catalyst. He obtained an absorption of 1530 ml. of hydrogen per g. of palladium present. Burrell and Oberfell[7] state that the method of Paal and Hartmann is very reliable. Taylor,[8] however, found that colloidal palladium solutions were unsatisfactory for the determination of hydrogen in low-temperature carbonisation gases. Beet[9] tried the solution of Paal and Hartmann for the determination of hydrogen in the Bone and Wheeler apparatus and reported that complete absorption is only obtained if the reagent is warmed to 50° C. Brunck[10] showed that 100 to 110 ml. of a solution containing 0·2 g. of palladium and 5 g. of sodium picrate could absorb 10 to 20 ml. of hydrogen in 5 minutes. Bonney and Huff[11] improved upon the Paal and Hartmann method by substituting sodium anthraquinone-2 : 7-disulphonate for sodium picrate, and obtained an absorption of 2708 ml. of hydrogen per g. of palladium. They also showed that the solution could be re-activated by passing oxygen through it.

Hofmann and Schneider,[12] Hofmann,[13] and Hofmann and Schibsted[14] investigated the use of noble metal catalysts activated by sodium chlorate solution, using mixtures of palladium chloride and osmium oxide, but found that the catalyst was easily poisoned by traces of carbon monoxide and that, prior to absorption, the residual gas had to be purified by passing it through an aqueous suspension of mercuric oxide and chromic acid.

Biesalski, V. Kowalski and Wacker[15] forced a mixture of hydrogen with an excess of oxygen under a pressure of 1·8 to 2 atmospheres through a foaming liquid containing palladous chloride as catalyst and various substances as anti-frothing agents, and found that 0·05 g. of palladous chloride could eliminate as much as 50 ml. of hydrogen in about 20 minutes. Later Biesalski and Giehmann[16] designed a contact candle of porous porcelain impregnated with a reduced noble metal and activated by a 25 per cent. solution of sodium chlorate, which was not poisoned by small quantities of carbon monoxide.

Hein and Daniel[17] used a solution of potassium permanganate and silver nitrate which they found to absorb hydrogen comparatively rapidly; the absorption was accelerated by introducing silvered silica gel into the pipette. Small quantities of oxygen were, however, evolved, and this necessitated the use of alkaline pyrogallol solution before the final reading was taken.

For various reasons, some of which have already been mentioned, none of the afore-mentioned methods has been adapted to routine gas analysis. In seeking a solution to this problem the following factors must be taken into consideration:

1. The absorbing medium should be capable of being dissolved or dispersed in a liquid of comparatively low vapour tension, preferably water, the confining liquid most commonly used in gas analysis.
2. For wide application the catalyst should be cheap and easily prepared in the laboratory. It should not be easily poisoned by carbon monoxide and it should have a fairly long life.
3. The absorbing medium should take up the hydrogen rapidly and completely, preferably at room temperature, and should have no action on the other constituents of the residual gas.

As the reaction sought was essentially a catalytic hydrogenation, we studied various substances capable of being hydrogenated at ordinary temperature and pressure in the presence of suitable catalysts. In this connection attention was first directed to the unsaturated organo-nitrogen compounds, as these appeared to be more likely to take up hydrogen at room temperature (*cf.* Ellis[18]). Several nitrogen-free organic compounds, such as cinnamic acid and oleic acid, were also tried, but found to be unsuitable. Of the compounds in the former category, comparative trials were made with *p*-nitrosophenol, α-nitroso-β-naphthol and dinitroso-resorcinol, and the last proved so superior to any of the compounds previously used or suggested, that it was used throughout this work as the absorbent. Further, *p*-nitrosophenol and α-nitroso-β-naphthol had a tendency to cause frothing. Dinitroso-resorcinol worked best in aqueous suspension; when dissolved in methyl alcohol or dilute alkali it did not prove so effective.

Several catalysts were investigated: although palladium proved to be more suitable than platinum, it had to be abandoned, as it was easily poisoned by traces of carbon monoxide, and on several occasions it suddenly became inactive without any assignable cause. Nickel catalysts, both supported and unsupported, were also tried; the latter did not prove to be of any value, but the supported catalyst was very satisfactory. The life of the catalyst, however, was short, but the technique of preparing it was so simplified, that this was relatively unimportant. In this connection Bosshard and Fischli[19] used a 3 per cent. suspension of reduced nickel in sodium oleate solution. The nickel was reduced at 340° C. and, according to these authors, difficulty was experienced in the reduction. Furthermore, the absorbing suspension had a tendency to froth, and, to overcome this difficulty, two pipettes were used—one for the absorption of the hydrogen, and the second, to which some alcohol had been added, to eliminate the foam. Anderson and Katz,[20] however, state that the method of Bosshard and Fischli is unworkable.

According to Thomas[21] (*cf.* Ellis[22]), when preparing nickel catalysts by reduction with hydrogen, the optimum activity is obtained by carrying out the reduction at approximately 300° C. for an unsupported catalyst, and between 350–500° C. when the nickel is supported on kieselguhr. Under the latter conditions he found that the activity was reduced to one-fifth when the reduction was carried out at 650° C., and that the nickel was practically inactive when reduced at 700° C. Gauger and Taylor,[23] in their work on the absorption of hydrogen, used similar temperatures for preparing the nickel catalysts.

In the course of the present work, however, it was found that nickel catalysts supported on kieselguhr, when reduced at 650–700° C., were more active than those prepared at 450° C., and, moreover, absorbed more hydrogen per unit weight of nickel than those prepared at the lower temperature by the method of Gauger and Taylor. Incidentally, the time required for reduction at the higher temperature was much shorter. It was also found that the catalyst was not poisoned by carbon monoxide, as was the palladium catalyst. A suspension of the nickel catalyst in conjunction with a suitable absorbent, *e.g.* dinitroso-resorcinol, absorbed hydrogen completely at room temperature (30° C.) from mixtures of hydrogen, nitrogen, methane, and ethane without affecting the other constituents of the gaseous mixtures.

EXPERIMENTAL

The hydrogen used in the experiments was prepared by the action of dilute hydrochloric acid on zinc. The gas was purified by passing it first through acidified silver nitrate solution, then through conc. sulphuric acid, and finally over solid caustic soda. When analysed in the Bone and Newitt apparatus, it gave 99·9 to 100 per cent. of hydrogen. It was found to be quite satisfactory for all the absorption determinations and also for the reduction of catalysts.

The absorption experiments were carried out in a Lunge-Orsat apparatus with five pipettes. The first four pipettes were for the absorption of carbon dioxide, oxygen, unsaturated hydrocarbons and carbon monoxide respectively, and the fifth for the absorption of hydrogen.

Preliminary experiments were instituted to investigate the technique of the absorption of hydrogen, and it was found that for rapid and complete absorption it was advisable to release frequently the vacuum produced in the pipette. This was carried out by dipping the lower limb of the pipette into the suspension of the absorbent, opening the tap, and allowing the suspension to enter the pipette at least every two minutes. The pipette was well shaken after each equalisation of pressure.

The dinitroso-resorcinol was prepared from commercial resorcin by the method given by Orndroff and Nichols.[24] The yield was theoretical and the product was used without further purification for all the absorption experiments.

NOBLE METAL CATALYSTS.—The following catalysts were prepared and examined:

No. 1. *Palladium chloride solution.*—0·05 g. of palladous chloride was triturated with a little water and made up to 50 ml. with water.

No. 2. *Palladium chloride in gum arabic emulsion.*—0·05 g. of palladous chloride and 0·5 g. of gum arabic were triturated with a little water and made up to 50 ml.

No. 3. *Reduced palladium supported on kieselguhr.*—1 g. of kieselguhr (Merck's) was washed with hydrochloric acid and macerated with 0·05 g. of palladous chloride. To this 2 ml. of formalin and a few drops of caustic soda solution were added, and the mixture was stirred for 15 minutes. Twenty ml. of 50 per cent. acetic acid were then added, and the mixture was filtered. The precipitate was washed first with dilute acetic acid and then with water and dried for 24 hours *in vacuo* over calcium chloride.

No. 4. *Palladium oxide.*—0·05 g. of palladous chloride and 1 g. of sodium nitrate were well mixed in a silica dish with a little water and evaporated to dryness, and the residue was heated strongly over a Bunsen flame for 5 minutes. After cooling, the mass was well ground, macerated with water and filtered, and the residue was washed with 1 per cent. sodium nitrate solution and dried *in vacuo* for 24 hours over calcium chloride.

No. 5. *Palladium oxide supported on kieselguhr.*—0·05 g. of palladous chloride, 1 g. of kieselguhr and 8 g. of sodium nitrate were well ground in a mortar with a little water. The mixture was transferred to a silica dish and evaporated to dryness, and the residue was heated strongly for 10 minutes. After cooling, the mass was macerated with 20 ml. of water and filtered, and the residue was washed with 1 per cent. sodium nitrate solution and dried *in vacuo* for 24 hours over calcium chloride.

No. 6. *Platinum chloride solution.*—0·08 g. of platinum was dissolved in 30 ml. of boiling *aqua regia*, the solution was evaporated to dryness, and the platinum chloride was dissolved in 100 ml. of water.

No. 7. *Reduced platinum in aqueous suspension.*—A rapid current of hydrogen was passed through 50 ml. of No. 6 at 80° C. In 30 minutes all the platinum was reduced to a fine powder.

TABLE 1

Absorption of hydrogen by dinitroso-resorcinol in presence of palladium and platinum catalysts

Expt. No.	Catalyst No.	Composition of absorption suspension			Time of absorption	Vol. of H_2 taken	Hydrogen absorbed		Hydrogen absorbed per g. of Pd.
		Amount of dinitroso-resorcinol g.	Water added ml.	Quantity of catalyst	Minutes	ml.	ml.	Per Cent.	ml.
1*a*	1	1·5	135	15 ml.	30	51	33·8	66·3	4000
1*b*	1	Repeated with same suspension			30	50·4	2·4	4·8	
2	2	1·5	135	15 ml.	30	50	30·6	61·2	3400
3	3	1·5	150	0·1 g.	15	49·8	18·0	36·3	6000
4*a*	3	1·5	150	0·3 g.	15	50·2	49·6	99·0	7000
4*b*	3	Repeated with same suspension			15	50·2	13·6	27·0	
5	3	3·0	150	0·6 g.	15	50·4	49·8	99·0	4000
5*b*	3	Repeated with same suspension			15	51·6	22·0	42·6	
6	4	1·5	150	0·015 g.	15	50·6	1·6	3·1	
7	5	1·5	150	0·3 g.	15	51·2	1·2	2·3	
8	6	1·5	135	15 ml.	15	50·0	1·4	2·8	
9	7	1·5	135	15 ml.	15	35·4	16·0	45·0	

It will be observed that reduced palladium supported on kieselguhr (catalyst No. 3) was by far the most active and the only one that gave results approximating to complete absorption. The activity, however, was greatly reduced after the catalysts had been once used.

In order to investigate the use of this catalyst in gas analysis a series of experiments was made to test its ability to absorb hydrogen from mixtures of hydrogen and nitrogen and of hydrogen and air. It was found, however, that while suspensions of the catalyst and dinitroso-resorcinol could absorb pure hydrogen almost quantitatively, when it was mixed with nitrogen the absorption was very incomplete.

This result may have been brought about by the presence of a small quantity of carbon monoxide in the nitrogen, as, according to Drakeley and Nicol,[25] carbon monoxide is produced when oxygen is absorbed by alkaline pyrogallol, and it was found that carbon monoxide poisoned the catalyst.

In the attempts to use it for the absorption of hydrogen from mixtures of hydrogen and air, anomalous results were obtained, the absorption in some experiments being as much as 110 per cent. This might be explained by the combination of some of the hydrogen with the oxygen of the air in the presence of the catalyst.

NICKEL CATALYSTS.—*Basic nickel carbonate supported on kieselguhr.*—20 g. of nickelous chloride, $NiCl_2,6Aq$. (Merck, cobalt-free) were dissolved in 100 ml. of water and 10 g. of finely-powdered kieselguhr (Merck), previously washed with hydrochloric acid, were added. The mixture was boiled for 15 minutes, after which a boiling solution of 20 g. of anhydrous sodium carbonate in 200 ml. of water was slowly added, with constant stirring, and the boiling was continued for a further 15 minutes. The mixture was then cooled and filtered, and the precipitate was washed free from chlorides, dried at 105° C., and stored in a stoppered bottle.

TABLE II

Absorption of hydrogen alone and hydrogen from mixtures of hydrogen and nitrogen by dinitroso-resorcinol in the presence of nickel-kieselguhr (1 : 2) *catalyst reduced at a low temperature* (450° *C.*). *Catalyst No.* 8.

	Composition of absorption suspension						
Expt. No.	Amount of catalyst g.	Amount of dinitroso-resorcinol g.	Water added ml.	Time of absorption Minutes	Volume of gas taken ml.	Absorption in ml.	Hydrogen absorbed Per Cent.
1	0·5	1·5	150	15	H. 49·4	31·0	62·8
2	0·5	1·5	150	30	H. 49·4	45·0	91·2
3	1·0	3·0	150	15	H. 48·2	48·0	99·5
4	1·0	3·0	150	30	H. 24·8 N. 27·2	24·4	98·5
5	1·0	3·0	150	30	H. 25·6 N. 23·8	25·6	100·0
6	1·0	3·0	150	20	H. 24·5 N. 23·5	24·5	100·0

Catalyst No. 8 (*nickel kieselguhr* 1 : 2, *reduced at* 450° *C.*).—About 4 g. of the above-mentioned basic nickel carbonate supported on kieselguhr were reduced in a Pyrex glass tube in a current of hydrogen at 450° C. for one hour. The tube was heated in an electric furnace, and the temperature was accurately controlled by means of a thermocouple. The catalyst, which was brownish-black, was cooled in a current of hydrogen and finally stored in a stoppered bottle.

Catalyst No. 9.—A similar quantity of basic nickel carbonate on kieselguhr was reduced at 700° C. as described above. The product thus obtained was black; it was stored in a stoppered bottle.

The results given in Tables III and IV show that, whilst both these catalysts, in conjunction with dinitroso-resorcinol, are quite effective in absorbing hydrogen either alone or from mixtures of hydrogen and nitrogen, the catalyst produced by reduction at 700° C. is the more active; furthermore, it can be used several times without losing its activity.

TABLE III

Absorption of hydrogen from mixtures of hydrogen and nitrogen by dinitroso-resorcinol in the presence of a nickel catalyst (nickel-kieselguhr) (1 : 2), *reduced at a temperature of* 700° *C. (Catalyst No.* 9.) *The suspension consisted of* 1·5 *g. of catalyst and* 3·0 *g. of dinitroso-resorcinol made up* 150 *ml. with water. In the experiments labelled (b), (c) and (d) the same absorption suspension is used as in the (a) experiment, showing that the suspension is capable of giving complete absorption even if used several times.*

Expt. No.	Time of absorption Minutes	Gas and vol. of gas taken ml.	Absorption ml.	Hydrogen absorption Per Cent.
1*a*	15	H. 26·2 N. 23·0	26·1	99·6
1*b*	15	H. 25·6 N. 23·0	25·4	99·3
1*c*	15	H. 24·2 N. 23·0	24·2	100·0
2*a*	20	H. 24·2 N. 23·4	24·2	100·0
2*b*	20	H. 24·8 N. 23·4	24·7	99·6
2*c*	20	H. 25·5 N. 23·4	25·5	100·0
2*d*	30	H. 24·8 N. 23·4	24·8	100·0
3*a*	25	H. 23·8 N. 24·2	23·8	100·0
3*b*	25	H. 23·8 N. 24·2	23·7	99·6
4*a*	15	H. 24·0 N. 24·0	23·8	99·2
4*b*	20	H. 23·8 N. 24·2	23·8	100·0
4*c*	20	H. 9·4 N. 24·6	9·3	99·0

As it was evident that the temperature at which the reduction was carried out could vary over a considerable range without detriment to the activity of the catalyst, experiments were instituted to simplify the technique of its preparation. The electric furnace and pyrometer were therefore dispensed with, and the heating was carried out by means of a Teclu burner. It was found that if the reduction was effected at a dull red heat (650–700° C.) for 10 minutes, a product was obtained (catalyst No. 10) which in appearance was similar to catalyst No. 9, and which proved equally effective for the absorption of hydrogen from mixtures of hydrogen and nitrogen.

APPLICATION TO GAS ANALYSIS.—A sample of town's gas, stored over saturated brine, was analysed for its hydrogen-content by the fractional combustion method, after removal of the carbon dioxide, oxygen, unsaturated hydrocarbons and carbon monoxide by the usual methods.

Two typical analyses of this gas were as follows:

	I Per Cent.	II Per Cent.
Carbon dioxide	5·5	5·3
Oxygen	1·4	1·4
C_nH_{2n}	1·1	1·1
Carbon monoxide	8·7	8·4
Hydrogen ..	29·9	35·1

It will be seen that the results for the various constituents, with the exception of the hydrogen, agree fairly well, but that the hydrogen varied from 29·9 to 35·1 per cent.

The residual gas from this sample was then treated with the dinitroso-resorcinol-nickel suspension. In each instance the contraction in volume was observed every 10 minutes and the minimum time for complete absorption was noted.

TABLE IV

Analysis of town's gas: Determination of hydrogen in the residual gas by absorption with a suspension of dinitroso-resorcinol and nickel-kieselguhr 1 : 2. *Catalyst No.* 10.

						Composition of absorption suspension						
Expt. No.	CO_2 Per Cent.	O_2 Per Cent.	C_nH_{2n} Per Cent.	CO Per Cent.	Residual gas Per Cent.	Catalyst g.	Dinitroso-resorcinol g.	Water ml.	Vol. of residual gas taken ml.	Time of absorption Minutes	Absorption ml.	Hydrogen in original gas Per Cent.
1	5·3	1·1	0·8	8·2	84·6	1·8	3	150	43·0	30	16·1	31·7
2	5·1	1·1	0·9	8·6	84·3	3·0	3	150	41·0	30	15·5	31·9
3	5·2	1·0	0·8	8·5	84·5	1·8	3	150	42·1	40	15·8	31·7
4	5·1	1·3	0·8	8·8	84·0	1·8	3	150	41·3	60	15·6	31·7
5	5·1	1·5	0·9	8·7	83·8	1·8	3	150	39·0	60	15·0	32·2

Although concordant figures were obtained in each instance for the percentage of hydrogen, the time required for complete absorption was too long for routine analysis.

Modification of the absorption suspension to improve the rate of absorption showed that increasing the amount of dinitroso-resorcinol was of little advantage. Considerable improvement was, however, effected by increasing the percentage of kieselguhr in the catalyst, so that it contained 4 parts of kieselguhr to one part nickel (catalyst No. 11), thereby providing a larger contact surface. The first tests in Table V were carried out with a catalyst of this kind. A further improvement consisted in using a freshly-prepared catalyst (No. 12), whereby the time of absorption was considerably reduced, as shown by the succeeding experiments in this table. The final catalyst (No. 12) was prepared as follows:—20 g. of nickelous chloride were dissolved in 200 ml. of water, and 20 g. of kieselguhr were added. This mixture was well ground in a mortar, diluted to 400 ml. and boiled for 10 minutes, and the nickel was precipitated as carbonate by addition of a boiling solution of 20 g. of anhydrous sodium carbonate in 200 ml. of water. After a further 10 minutes' boiling, the mixture was cooled and filtered. The precipitate was washed free from chloride, dried at 105° C., and finely powdered. It was reduced at dull red heat as required, cooled in a current of hydrogen, and added directly from the reduction tube to the dinitroso-resorcinol suspension.

TABLE V

Analysis of town's gas : Determination of hydrogen in the residual gas by absorption with a suspension of dinitroso-resorcinol nickel-kieselguhr (1 : 4). *Catalysts Nos.* 11 *and* 12.

		Analysis of gas					Composition of absorption suspension						
Expt. No.	Catalyst No.	CO_2 Per Cent.	O_2 Per Cent.	C_nH_{2n} Per Cent.	CO Per Cent.	Residual gas Per Cent.	Catalyst g.	Dinitroso-resorcinol g.	Water ml.	Vol. of residual gas taken ml.	Time of absorption Minutes	Absorption ml.	Hydrogen in original gas Per Cent.
1*a*	11	5·5	1·4	0·6	8·7	83·8	3	3	150	37·5	20	14·5	32·4
b							Same suspension after 3 hours			24·3	20	9·2	31·7
2*a*	11	5·4	1·2	0·9	8·7	83·8	2	3	150	31·3	20	12·1	32·4
b							Same suspension after 3 hours			30·8	20	11·8	32·1
c							Same suspension after 6 hours			29·3	20	11·1	31·7
3*a*	12	5·4	1·0	0·8	8·6	84·2	1·5	1·5	150	20·6	10	7·8	31·9
b							Same suspension after 3 hours			20·4	10	7·8	32·2
4*a*	12	5·3	1·4	1·1	8·4	83·8	3	3	150	19·1	5	7·3	32·0
b							Same suspension after 3 hours			19·4	5	7·4	32·0

DETERMINATION OF HYDROGEN IN THE PRESENCE OF METHANE.—A sample of methane, prepared from sodium acetate and soda-lime, was found to contain:—CO_2, 0·5; O_2, 1·5; C_nH_{2n}, 5·2; CO, trace; residue, 92·8 per cent. It was purified by absorption of the carbon dioxide and oxygen in alkaline pyrogallol, and of hydrocarbons in fuming sulphuric acid. The analysis of the residual gas gave:—$CH_4 + H_2$, 93·3; N_2 (by diff.), 6·7 per cent.

Twenty-four ml. of this gas were shaken with the nickel-kieselguhr dinitroso-resorcinol suspension and showed an absorption of 0·9 ml. of hydrogen = 3·6 per cent.

The residual gas from this sample was mixed with 24 ml. of hydrogen and again treated with the absorption suspension.

Twenty-four ml. = 100 per cent. of the hydrogen was absorbed.

The methane and nitrogen were unaffected, thus showing that hydrogen in a mixture of hydrogen, methane and nitrogen can be rapidly and accurately determined.

DETERMINATION OF HYDROGEN IN THE LOW TEMPERATURE (600° C.) ASSAY GAS FROM X SEAM JHARIA COAL.—The complete analysis of this sample, carried out in an hour and a half, gave the following results:—CO_2, 3·0 (by vol.); O_2, 0·8;

C_nH_{2n}, 0·8; CO, 4·0; H_2, 37·2 (by absorption; C_nH_{2n+2}, 51·7 ($n = 1·05$); N_2, 2·5 (by diff.) per cent.

The method has thus been found to give satisfactory results even when the hydrogen is present as a constituent of a complicated mixture such as town's gas or carbonisation assay gas.

SUMMARY:—Numerous methods have been proposed for the determination of hydrogen in mixtures of hydrogen with saturated hydrocarbons and nitrogen by absorption. None of those methods, however, has been found suitable for the determination of hydrogen in coal-gas analysis.

A simple and effective method has been evolved for this purpose whereby the hydrogen in the residual gas is absorbed rapidly and completely by means of an absorption medium consisting of an aqueous suspension of dinitrosoresorcinol in the presence of a freshly reduced nickel catalyst supported on kieselguhr. Contrary to the experience of other workers, it has been found that basic nickel carbonate when reduced at a dull red heat (650–700° C.) proves to be an active catalyst. The estimation was carried out at ordinary temperature in a Lunge–Orsat apparatus provided with a fifth absorption pipette. The catalyst was not poisoned by traces of carbon monoxide.

One of us (H. N. Banerjea) thanks the University of Bombay for a Research Fellowship which enabled him to take part in the investigation.

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DEPARTMENT OF CHEMICAL TECHNOLOGY
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A New Process for the Separation of Selenium and its Determination in Lead Alloys*

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THE work which forms the subject of this paper was undertaken on account of a request to determine selenium occurring as a minor constituent of lead-antimony alloys. The problem at first sight seems simple, for selenium can be precipitated as metal by reducing agents. On attempting this, however, I encountered various complications. By far the most convenient solvent for fairly large samples of lead is nitric acid; the presence of antimony necessitates citric acid as well; the precipitation of selenium in this acid liquid proved to be most uncertain, as selenium dissolves fairly readily in nitric acid; furthermore, the use of sulphur dioxide as reducing agent provoked the precipitation of large amounts of lead sulphate. The small quantities of selenium present made it desirable to use a volumetric method and that of Coleman and McCrosky[1] was tried. This method relies on the solubility of selenium in potassium cyanide solution, but it soon became apparent that it seemed practically impossible to induce the whole of the selenium to go into solution when at last one had succeeded in precipitating it. To judge by the colour, the grey modification of selenium is soluble in potassium cyanide solution and the red insoluble, and, although the red tends to change into the grey, some red residue remained on the filter even after the precipitate had been allowed to stand for a considerable time. In view of these difficulties the direct precipitation of elemental selenium was abandoned. The Reinsch reaction has been shown to be effective in the complete deposition of antimony from hydrochloric acid solution,[2] and of mercury from nitric acid solution[3]; antimony is not deposited at all from nitric acid. On trial of the Reinsch reaction on selenium it was found that while, as might be expected, it gave ready deposition from hydrochloric acid (which was valueless when dealing with a lead antimony alloy), it was also deposited from a nitric acid solution, but the film, which was readily stripped off the copper as the reaction proceeded, seemed to show a tendency to redissolve in the nitric acid. Solution of many of the metals in nitric acid can be inhibited by addition of urea; this was therefore next tried, with very satisfactory results, complete deposition of the selenium being obtained; lead nitrate seemed to have no action whatever on the reaction, and antimony dissolved in a nitric-citric-acid mixture neither yielded a deposit itself nor prevented the selenium from depositing. The film so obtained is grey-black in colour; it dissolves instantly and completely in potassium cyanide solution and obviously consists of a copper selenide (*vide infra*). The separation of the selenium from the lead and antimony having been achieved, the next problem was that of determination. At first it was assumed to be necessary to separate the selenium from copper, and a good deal of work was undertaken to this end; the separation could be effected readily enough, but the selenium so obtained was by no means readily or completely soluble without oxidation. As the results obtained were entirely unsatisfactory, it seemed worth while to find out what sort of result would be obtained by carrying out Coleman and McCrosky's titration on the solution resulting from the cyanide stripping of the film itself. It was fully anticipated that, as the film obviously contained a large proportion of copper and as this would dissolve in cyanide in the cuprous condition, the copper would use up potassium iodate in the titration and so influence the figure obtained. This anticipation was not borne out in practice; the results, far from being high in proportion to the copper present, tended actually to be low when the ordinary factor was used. Coleman and McCrosky's method is as follows:—To the cyanide solution of the selenium is added gum arabic followed by a large excess of strong hydrochloric acid, and air is then bubbled through the liquid for ten minutes; during this time the solution gradually turns an orange colour owing to the liberation of colloidal selenium. At the end of the bubbling hydrocyanic acid has been sufficiently removed to have no influence on the titration, which is now carried out with $M/60$ potassium iodate solution; the reactions involved are given as:

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* Communication from the Research Department, Woolwich.

$$5Se + 4KIO_3 = 2K_2SeO_3 + 3SeO_2 + 2I_2$$

$$2I_2 + KIO_3 + 6HCl = 5ICl + KCl + 3H_2O$$

It will be noticed that the selenium is oxidised to H_2SeO_3 and an equivalent amount of iodine is set free; the latter is then oxidised to ICl. The iodate is run in until the selenium colour has disappeared and the iodine colour is mostly discharged; 4 ml. of carbon tetrachloride are added, which on shaking should be coloured violet; titration is then continued with vigorous shaking until the violet colour of the carbon tetrachloride is just discharged. On treating the cyanide solution of the film in this manner a more or less dark greenish-brown colour is produced immediately the hydrochloric acid is added; on bubbling air this colour, which is presumably due to copper selenide, becomes progressively paler and redder until it finally reaches the orange-scarlet colour of selenium. The copper is probably oxidised by the air-bubbling, for it does not interfere in any way in the titration beyond producing in the liquid a greenish-yellow colour which must not be mistaken for iodine. This titration, as has been mentioned earlier, gave low (sometimes very low) results with the solutions obtained by stripping the films; this was eventually traced to the strength of the hydrochloric acid present during the air-bubbling. A high concentration of hydrochloric acid is necessary in the titration, and apparently in Coleman and McCrosky's experiments it gave no trouble in the preliminary air-bubbling, but in the Reinsch film solutions the copper presumably acted as a catalyst for the oxidation of the selenium, and occasionally hardly any selenium colour was produced. It was found that if only 10 ml. of hydrochloric acid were added to the solution after stripping and the liquid was then submitted to air-bubbling, no apparent oxidation of the selenium took place; after bubbling, the hydrochloric acid could be made up to the required strength without ill effects and the titration finished as usual. The acid strength recommended by Coleman and McCrosky seems to be too low, as there is usually a slight separation of powdery selenium, and this appears to be only slowly dissolved at the lower acid concentration. The technique finally adopted was to add sufficient strong hydrochloric acid to the liquid, after bubbling, to make the volume present three-fifths of the whole volume. The complete method is as follows:

PROCESS.—The selenium solution in approximately 10 per cent. nitric acid is treated with about 2 g. of urea, and a slip of copper, about 1 × 1½ in., cleaned by previous warming in dilute nitric acid, is dropped in. The liquid is heated to boiling point and then allowed to stand for half-an-hour on the steam-bath (directly over the steam); it is then boiled for ten minutes and cooled. The liquid is filtered through a small paper filter and the beaker is well rinsed in, but the copper slip is retained in the beaker; the filter is next thoroughly washed with cold water, the copper slip in the beaker being meanwhile covered with a layer of water to prevent excessive oxidation. The funnel holding the filter having been placed over a clean Erlenmeyer flask (capacity 600 ml.), a few drops of a saturated solution of potassium cyanide are added to the water in the beaker containing the copper; this should cause immediate solution of any film remaining on the copper or adhering to the beaker. The solution in the beaker is then poured through the filter in small portions at a time, care being taken that all the precipitate is dissolved; a minute amount of black or brownish material is generally left undissolved, but this is probably due to an impurity in the copper and does not contain selenium. The beaker having been rinsed in, the filter is given five small washes with cold water; it is desirable to keep the volume down, as this minimises the amount of hydrochloric acid to be added subsequently. About 2 ml. of gum arabic solution (1 per cent.) are added to the filtrate, which should then be roughly measured; 10 ml. of hydrochloric acid are added and a rapid stream of air is bubbled through it for 15 minutes, the flask being tilted to allow the air to pass through a maximum depth of liquid. The colour should now be a golden brown (due to the holding of the scarlet selenium in colloidal solution by the gum arabic); larger amounts of selenium may give a red or orange haze. The remainder of the hydrochloric acid is then added; the volume required is that necessary to bring the total amount of acid (including the 10 ml. already present) to 1½ times the measured volume of the filtrate, so that the solution now contains three-fifths of its volume of strong hydrochloric acid; the liquid is then titrated with $M/60$ potassium iodate solution without undue delay. As the potassium iodate solution is run in selenium is oxidised and iodine liberated; the colour change is therefore not very marked during the first part of the titration; after addition of four-fifths of the total iodate required the selenium is (or should be) all oxidised and the iodine begins to be converted into iodine monochloride; the colour therefore lightens rapidly. The titration should be pushed as far as is safe before adding the carbon tetrachloride, because traces of selenium seem sometimes to resist oxidation rather strongly, and if the tetrachloride is added before they are all dispersed they are drawn into the interface, where they are neither so easily seen nor so readily oxidised as the iodine. The end-point of the titration is of course that at which the carbon tetrachloride is just decolorised. During the initial titration it must be borne in mind that, copper being present, the colour of the fully oxidised solution is not white but greenish-yellow proportionate to the amount of selenium present; this colour does not introduce any difficulties, as it is only marked with higher amounts; with 0·002 g., or less, it is so faint as to be practically invisible. With 0·001 g., or less, of selenium it seems impossible to avoid getting selenium in the tetrachloride interface, as it is unsafe to carry the initial titration sufficiently far to oxidise it completely; in these circumstances it is still possible to get an accurate titration, but the end-point must be approached slowly and more cautiously, and shaking must be more vigorous.

$$1{\cdot}0 \text{ ml. of } M/60 \ KIO_3 \equiv 0{\cdot}001317 \text{ g. of Se.}$$

The amount of carbon tetrachloride to be added is 4 ml.

The process was tested, with the following results.

(*a*) *Selenium alone; separated from* 10 *per cent. nitric acid solution by the Reinsch reaction.*

Selenium taken g.	Titration ml. of $M/60$ KIO_3	Selenium found g.
0·0010	0·75	0·00099
0·0020	1·50	0·00198
0·0030	2·30	0·00303
0·0040	3·05	0·00401
0·0050	3·85	0·00507
0·0070	5·25	0·00692
0·0100	7·40	0·00975

(*b*) *Selenium in Lead-Selenium Alloys.*—Five g. were dissolved in 30 ml. of dilute nitric acid (sp.gr. 1·2) + 30 ml. of water, and sodium hydroxide was added until a permanent precipitate was formed, and this was then just taken up by addition of nitric acid. Ten ml. of strong nitric were added in excess followed by 2 g. of urea. The Reinsch separation was then carried out.

Lead taken g.	Selenium taken g.	Titration ml. of $M/60$ KIO_3	Selenium found g.	Per cent. of selenium	
				taken	found
5·0	0·0020	1·50	0·00198	0·0400	0·0396
5·0	0·0040	3·05	0·00402	0·0800	0·0804
5·0	0·0060	4·55	0·00600	0·1200	0·1200
5·0	0·0080	6·05	0·00797	0·1600	0·1594
5·0	0·0100	7·55	0·00995	0·2000	0·1990

(*c*) *Selenium in Lead-Antimony-Selenium Alloys.*—Five g. were dissolved in 30 ml. of dilute nitric acid (sp.gr. 1·2) + 30 ml. of water + 10 ml. of citric acid solution (100 g. dissolved in 200 ml. of water). The liquid was not neutralised after solution, but 5 ml. of nitric acid (conc.) + 15 ml. of water were added followed by 2 g. of urea. The Reinsch process was then carried out.

Lead taken g.	Antimony taken g.	Selenium taken g.	Titration, ml. of $M/60$ KIO_3	Selenium found g.	Per cent. of selenium	
					taken	found
5·00	0·15	0·0020	1·50	0·00198	0·0388	0·0385
5·00	0·15	0·0040	3·10	0·00408	0·0776	0·0792
5·00	0·15	0·0060	4·50	0·00593	0·1164	0·1152
5·00	0·15	0·0080	6·05	0·00797	0·1553	0·1548
5·00	0·15	0·0100	7·60	0·01001	0·1942	0·1944

COMPOSITION OF THE REINSCH FILM.—As it seemed desirable to know the composition of the deposit formed in the Reinsch reaction carried out as described above, an analysis of the film was made. The deposit obtained from 0·100 g. of selenium was thoroughly washed with water, then with alcohol and finally with ether, dried at 110° C., detached as far as possible from the copper and weighed; the weight obtained was 0·258 g. (Cu_2Se would require 0·2613 g.). Copper was determined on 0·1005 g. of this substance by dissolving, removing selenium by precipitation, and determining the copper electrolytically; selenium was determined by simply dissolving 0·0509 g. in potassium cyanide solution and titrating according to the method given above; the results obtained, compared with those required for Cu_2Se, were as follows:

	Obtained by analysis Per Cent.	Required for Cu_2Se Per Cent.
Copper	61·4	61·7
Selenium	37·9	38·3
	99·3	100·0

It therefore appears that the compound formed in the Reinsch reaction with selenium is Cu_2Se; this, from other considerations, is the compound most likely to be formed.

An attempt to determine selenium gravimetrically in this manner was unsuccessful, as it seemed impossible completely to detach the film from the copper, and results obtained were from 1·5 to 4 mg. low.

It would be obviously advantageous if tellurium could be separated from lead-antimony-tellurium alloys in the same way as selenium; this has been tried, but so far without conspicuous success. The Reinsch reaction appears to stop when a small proportion of the tellurium has been deposited; whether this is due to the tellurium completely coating the surface of the copper (the tellurium film, in contrast with that of selenium, is strongly adherent) and so stopping further action, or whether the oxidising action of the nitric acid is too strong, or the acid strength too high, is not yet apparent.

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Cacao Shell in Cocoa and Cacao Products

By H. C. LOCKWOOD, B.Sc., F.I.C.

(*Read at the Meeting, November* 2, 1938)

The determination of cacao shell in cocoa and cacao products with any degree of accuracy is a matter of extreme difficulty. Considerable attention has been given to the subject by many chemists, but their conclusions and views are controversial. It is, however, generally agreed that it is impossible to detect minute traces of shell in the finely-ground product produced by modern machinery—much less attempt an actual determination. Only when there is at least 1 per cent. can its presence be established with any degree of certainty. The modern winnowing machines produce a cacao nib virtually free from shell, and it is in the interest of manufacturers of the best qualities of cocoa and chocolate to attain this refinement, as the flavour and smoothness of the finished products are considerably impaired by the inclusion of shell.

The question under review attracted critical attention in 1918 owing to the issue of the Cocoa Powder Order. The Order provided that after April 8th, 1918, no cocoa powder must be manufactured which contained more than 5 per cent. of cacao shell, the cacao butter content being between the limits 22·5 and 30 per cent. This was known as "Grade B Cocoa Powder," whereas the Grade A material was not allowed to contain more than 2 per cent. of shell. These specifications were severely criticised by Public Analysts and chemists concerned with the manufacture of cocoa and chocolate. The limits prescribed were shown to be impracticable, and representations to this effect were made by this Society to the Ministry of Food.

Since 1895 numerous methods have been proposed by various workers for the estimation of shell in cocoa, but those dealing with crude fibre have been generally the most successful. This investigation has been mainly concerned with improvements in the determination of crude fibre and the interpretation of the results for shell estimation.

Crude Fibre.—For the determination of crude fibre several processes and modifications, involving the use of various reagents, have been proposed. One of the earliest methods was devised by König,[1] who used glycerol and sulphuric acid. The principle was investigated by Matthes and Müller,[2] Crossfeld,[3] and the Swiss official laboratories.

A number of modifications have been proposed by various workers, and the principle is incorporated in the official method of the Association of Official Agricultural Chemists, U.S.A.[4] I have closely studied each step in this process, and have devised a strictly standardised procedure, which has been found to give excellent duplicate results by the same or a different operator.

Preparation of Sample.—The preparation of the dry fat-free material with particles not exceeding a certain size is a matter of great importance in crude fibre determination. Cocoa powders on the market to-day are generally sieved in course of manufacture and, on examination, will be found to pass, to a great extent, through a No. 10 sieving or bolting silk, the size of the apertures being, on an average, 0·145 mm. (0·0056 in.). It was decided that all material used for fibre determination should be of sufficient fineness to pass through silk of this texture, as it would aid complete extraction of the fat and give the most suitable particle size for the action of acid and alkali. It is obviously impracticable to sieve material containing a high percentage of cocoa butter, such as ground beans, nib or mass, *i.e.* the commercial product. Such materials should be finely divided and then partly defatted by dissolving them in warm petroleum spirit and filtering on a Buchner funnel. The residue is then dried and mixed, and a suitable quantity is completely sieved through a No. 10 bolting silk by grinding any residue by hand. Five to seven g. are then extracted in a Soxhlet apparatus and dried in the water-oven. Cocoa powder is treated in the same way as the partly extracted material.

The effect of size of particles on the fibre result was discussed by Knapp and McLellan,[5] who, when using roasted nibs of varying degrees of fineness, obtained the following range of percentages: very finely ground, 5·9 to 6·5; finely ground, 7·3 to 8·5; slightly coarser, 9·3 to 11·6. The size of the particles was comparable with cocoa powders of commerce in 1918, and they suggested that the difficulty with which the fat is extracted from the larger particles accounted for the high results obtained with coarse material. In my experience, however, with pure cocoa nib, sieved through a No. 10 silk, the results (5·6 per cent.; see Table III) were identical with those obtained when the material was passed through a No. 19 silk, the size of the apertures being those specified for British Standard Sieves Nos. 100 and 200, respectively. It was considered, therefore, that a No. 10 bolting silk or a 100 B.S.S. sieve could be used as a standard.

The Apparatus.—The use of ground-joint assembly has been found to be a great advantage, in that during the occasional mixing, later recommended, the splashing of material up to the neck is of little consequence, as the glass is washed by the condensate. Rubber or cork is disintegrated by the hot acid and alkali and tends to contaminate the product.

Weighing and Measuring.—In weighing out the material for the determination of fibre, it was found that the freshly-dried product absorbed moisture very readily from the atmosphere. This was particularly noticeable with shell, and speed in weighing was essential. The error in duplicate determinations may amount to 2 per cent. of the result, especially when the second determination is made a day or so later on the dry material kept in a stoppered bottle or ordinary desiccator. For this reason it is important that the fat-free material should be freshly dried before use.

It was observed that if the weighed material was transferred to a dry flask and water was added, a compact mass formed on the bottom of the flask, and could be dispersed only after several minutes' mixing. It is evident that if the heating is started with a conglomerate mass on the bottom, there is a distinct possibility of vitiating the result. This is overcome as described under Procedure (*q.v.*).

Prevention of Frothing.—In the determination of fibre it was found that during the boiling with acid under reflux frothing was liable to occur only for the first minute, whilst in the boiling with alkali there was risk of excessive frothing for about 15 minutes, and constant application of a wet cloth was usually required.

It was felt that an error might be introduced here, some points of argument being in favour of a higher, others of a lower result. Amyl alcohol was eventually tried as an anti-frothing agent, and the following procedure, which prevented all serious frothing, was adopted:—Two ml. of amyl alcohol were added to the cold acid mixture, which was boiled and filtered, and the residue was washed in the usual way. Two ml. of amyl alcohol were also added to the alkali mixture. The residue was filtered off and washed with hot water, then twice with 50 per cent. industrial spirit (100 ml. in all), and finally with water.

Table I gives the comparative results obtained with normal and excessive frothing and those obtained with the use of amyl alcohol.

TABLE I

Type of cocoa	Normal frothing g.	Excessive frothing g.	With amyl alcohol g.
(A) Treated* ..	0·120 0·119	0·117	0·121 0·121
(B) Treated ..	0·120	0·117	0·120 0·120
(C) Untreated	0·119	0·117	0·120

* Finely ground cacao nib which has been treated with an alkaline salt for the preparation of "soluble" cocoa.

The results in the first and last columns show excellent agreement and the addition of amyl alcohol is therefore recommended with confidence. The lower results in the middle column are due undoubtedly to the enhanced action of the superheated mixture prior to frothing.

According to the A.O.A.C. method,[4] a current of air can be used to reduce the frothing, but this has been found not very successful, and, being optional, introduces an alternative which, under certain conditions, may influence the results to a considerable degree.

Filtering After Acid Treatment.—In the A.O.A.C. method linen is used for the first filtration, and their specification states that Butcher's linen or dress linen with about 45 threads to the inch, or, alternatively, No. 40 filtering cloth, made by the National Filter Cloth and Weaving Company, or its equivalent, may be used. Such a number of alternatives, or in fact any alternatives, are undesirable in a process of this nature if concordant results are required.

The use of copper gauze as a filtering medium was suggested by Fairley and Burrell,[6] who recommended a gauze having 100 meshes to the linear inch. They obtained lower results than when using fine linen, and an even finer gauze would have to be manufactured before this modification could be practicable. In fact, Knapp and McLellan[5] considered fine linen somewhat unsuitable as a filtering medium for cocoa material owing to the extreme fineness of the cocoa particles, and preferred ordinary filter-paper, such as 12·5 cm. Swedish or Whatman No. 1. The size of the filter-paper has, with advantage, been increased to 15 cm., and the paper should be folded in a simple quarto manner to simplify washing and subsequent transference. A hardened fast-filter-paper, such as Whatman No. 541, has been found very satisfactory.

Treatment with Alkali.—After the residue has been washed with hot water until virtually free from acid, it is returned to the flask as described under Procedure (*q.v.*), 180 ml. of hot water being used.

Twenty-five ml. of 10 per cent. sodium hydroxide solution are added to make a 1·25 per cent. solution. It is recommended that this solution should be prepared accurately, *i.e.* adjusted to 2·5 *N*. Previously, little attention has been given to this point; in fact, Knapp and McLellan[5] state: "Rinse the substance back into the flask with not more than 200 c.c. of water (use hot water if preferred) and add 2·5 g. of sodium hydroxide (stick, flake or other form, provided it is pure and approximately 98 per cent. strength)." They considered that within narrow limits the strengths of the sulphuric acid and sodium hydroxide solution used were of little importance. This opinion was modified subsequently, and the accuracy of the strength of the alkali was found to be more important than that of the acid. For the acid strength Whymper[7] gives 200 c.c. of water with 2·5 c.c. of conc. sulphuric acid instead of 2·5 g., and divergencies of this nature obviously lead to incompatible results.

Collecting the Crude Fibre.—According to the official method of the A.O.A.C.[4] three types of filters can be used, *viz.* a Gooch crucible with an asbestos mat, an alundum crucible, or linen. If the last is used the residue is later transferred to a prepared Gooch crucible having a thin but close layer of ignited asbestos. The procedure outlined by Knapp and McLellan,[5] using filter-papers, is, however, much to be preferred, and a technique has been evolved from their idea (see Procedure).

The speed with which the manipulation can be executed is greatly in its favour. It is obviously advisable to remove the hot sodium hydroxide in the shortest possible time after the prescribed 30 minutes has elapsed, and this is not practicable if a Gooch or similar crucible, having a small effective area, is used. In a Gooch crucible the crude fibre builds up a layer of low permeability and 15 minutes may elapse before filtration of the 200 ml. is complete, whereas half-a-minute is ample time when filter-papers and moderate suction are used. It is to be regretted that the filter-paper method has not received recognition.

RECOMMENDED METHOD:—*Preparation of Sample.*—The material is prepared in a fat-free condition and sieved through a No. 10 silk, *i.e.* No. 100 British Standard Sieve, as previously described.

Procedure.—Two 12·5-cm. Swedish filter-papers are dried in the steam-oven so as to be ready for use. The dry fat-free material is transferred from the oven to an efficient desiccator and allowed to cool for 20 to 30 minutes. Cold water (190 ml.) is measured in a cylinder, and about 100 ml. are poured into a 500-ml. conical flask having a No. 3 ground neck, a funnel being used to keep the sides of the flask dry. Exactly 2 g. of the dry fat-free material are weighed rapidly and transferred to the flask. The remainder of the water in the cylinder is used to wash down any cocoa clinging to the side of the flask. Ten ml. of sulphuric acid (25 per cent. by weight) are added while the flask is gently rotated, and 2 ml. of amyl alcohol and two small pieces of broken porcelain are introduced to prevent frothing. The flask is connected with a vertical condenser having a No. 3 joint at the end, and the joints are wetted with a few drops of water before being tightened together.

The contents of the flask are heated to boiling as rapidly as practicable, and when boiling begins the time is noted, the burner is lowered and the flask is gently rotated. After boiling has continued for about two minutes the liquid is splashed up the side of the flask to remove any clinging particles deposited by the initial boiling. This manipulation is repeated three or four times while refluxing. At the end of exactly 30 minutes' boiling, the flask is disconnected and its contents are filtered through a 15-cm. No. 541 Whatman filter-paper (folded in the quarto way) which has been wetted with water. The rate of filtering can be increased by using two folded filter-papers, one placed inside the other to give four thicknesses all round. The second paper should be fast-filtering, but of a lower quality than the hardened one. The flask and filter-paper are washed twice with hot water, the filter-paper being allowed to drain well before each washing.

The residue is transferred to the flask in the following way:—A small wash-bottle, holding about 500 ml. and fitted in the usual way, is partly filled with water and then drained through the mouth-piece; 180 ml. of hot water, equivalent to 175 ml. of cold water, are introduced and used, in a very gentle stream, to wash the cocoa from the opened filter-paper. The wash-bottle is finally drained through the mouth-piece and so delivers the measured volume.

The contents of the flask are heated to boiling, and 25 ml. of 10 per cent. sodium hydroxide solution are added, together with 2 ml. of amyl alcohol. The flask is re-connected with the reflux condenser and heated quickly to boiling. From this point the procedure is the same as when boiling with acid. After exactly thirty minutes' boiling, the contents of the flask are filtered without delay on a 9-cm. Buchner funnel through the two previously dried 12·5-cm. Swedish filter-papers, of which the top one, being the heavier, has been weighed, the lighter one being used on the weight-pan of the balance. The outer edges of the filter-papers are turned up uniformly so as to form a container inside the Buchner funnel. The residue is washed twice with boiling water, and the jet of water is then directed round the edge of the filter-papers. The washing is continued with 100 ml. of 50 per cent. industrial spirit in two portions, and finally with hot water, care being taken to remove all traces of alkali from the edge of the filter-papers. After being dried in the oven to constant weight, the paper containing the fibre is ignited in a platinum dish, and the ash is subtracted from the previous weight of fibre. The percentage is then calculated on the dry fat-free material, and recorded as fibre percentage.

By using the foregoing technique and observing all the precautions mentioned, the results in Table II were obtained with cacao grown in West Africa.

Examination of these results shows that there was close agreement in duplicate or triplicate determinations, the maximum divergence being 0·2 per cent. for nib and 0·3 per cent. for shell. The results also show that there has been no material change in the fibre-content of cacao nib and shell since Knapp and McLellan's paper in 1919; hence, although the fibre from the nib is slightly lower, and that from the shell somewhat higher, it is proposed to retain the standards of 5·8 and 18·5 per cent. suggested by these authors.

It is interesting to note that cacao from various places in West Africa, *e.g.* Accra, Kumasi and Nigeria, all give the same figure—5·6, and that this is the same even for superfine material that has passed through a No. 19 sieve. The treatment of cocoa mass, which was carried out on a small scale, has very little influence on the amount of fibre, and only a further slight decrease, of the order of 0·1 per cent., was produced when the mass was made into pressed cake in a small experimental press. With regard to shell, the results confirm those of Knapp and McLellan when using the A.O.A.C. method, *viz.* that the particle size after a certain limit of fineness has no influence on the fibre figure.

TABLE II

FIBRE RESULTS ON DRY FAT-FREE MATERIAL

Source	Material and treatment	Passed through sieve*	Fibre Per Cent.
Accra	Nib, as untreated mass ..	No. 10	5·7; 5·6; 5·6
	Nib ,, ,, ,, ..	,, 19	5·6
	Pressed cake from untreated mass	,, 10	5·5
	Nib, as treated mass	,, 10	5·6; 5·4; 5·5
	Pressed cake from treated mass ..	,, 10	5·4; 5·4
	Shell	,, 10	19·5; 19·5
	,, ...	,, 19	19·8; 19·5
	,, ...	,, 10 but not No. 19	19·6; 19·4
Kumasi	Nib, as untreated mass ..	No. 10	5·6; 5·6
	Shell	,, 10	18·4
Nigeria	Nib, as untreated mass ..	,, 10	5·5; 5·5; 5·7
	Shell	,, 10	19·7; 19·4

*Nos. 10 and 19 silks are equivalent to British Standard Sieves Nos. 100 and 200 respectively.

It might appear from the figures recorded in Table II that the determination of traces of shell in cocoa material should be fairly straightforward and capable of quite accurate results. This would possibly be so if only African-grown cocoa had to be considered, but appreciable variations occur in cocoa grown in different countries. Using the A.O.A.C. method, Booth, Cribb and Richards[8] obtained 4·7 to 6·2 per cent. for roasted nib and 13·2 to 16·3 per cent. for roasted shell, whereas Winton, Silverman and Bailey[9] recorded 4·7 to 6·6 per cent. for roasted nib and 13·7 to 20·7 per cent. for shell. The results in Table III were obtained by the improved technique previously described. The average weight of bean and the shell percentage on bean are also included.

With a variation of 5·5 to 6·6 per cent. in the fibre in cacao nibs from various sources, it would seem that the method has little practical application. This may be so for cacao of unknown origin, but for a manufacturer's own products, when the type of bean is known, the fibre figure can be of definite value for determining the amount of shell present. The average of the fibre figures for nib is 5·9 per cent., and this agrees with the Knapp–McLellan result of 5·8 per cent.

The results obtained with shell vary from 15·5 to 19·5 per cent., but, if Arriba and Grenada products are omitted, the figures lie between 17·8 and 19·5. The average of all the fibre figures for shell comes to 18·2 per cent., and this is in close agreement with the 18·5 per cent. taken by Knapp and McLellan.

TABLE III

Source	Av. weight of bean g.	Shell on bean Per Cent.	Fibre in fat-free material	
			Nib Per Cent.	Shell Per Cent.
Accra	1·050	11·1	5·6	19·5
Kumasi	1·065	11·5	5·6	18·4
Nigeria	1·084	10·7	5·6	19·5
Arriba	1·405	11·1	6·3	15·5
Grenada	1·030	14·8	6·5	16·5
Bahia	0·967	12·8	5·5	17·8
Samoa	1·120	8·8	5·7	18·5
Trinidad	1·091	13·5	5·8	17·9
Jamaica	1·034	8·0	6·2	19·5
Ceylon	1·149	7·9	6·6	19·3

The beans in Table III had been roasted commercially, some being heated more than others, according to whether they were intended for cocoa or chocolate. To ascertain the effect of the degree of roasting on fibre results, samples of raw beans were obtained and 7-lb. lots were roasted in an experimental machine. For low roast, approximately 30 minutes' heating was given, after which time the temperature had risen to 115° C., whilst high roast reached 145° C. in 40 minutes. The experimental roaster was heated externally with gas, whereas internal gas heating is practised commercially, and hence the figures in Tables III and IV do not stand too strict comparison. Seasonal variations will also account for divergencies.

TABLE IV

Country of origin	Raw		Low roast 115° C.		High roast 145° C.	
	H.C.L.	D.M.L.	H.C.L.	D.M.L.	H.C.L.	D.M.L.
NIB						
West Coast of Africa (1) ..	5·2	5·25	5·5	—	5·5	—
(2) ..	5·3	5·3	—	—	6·0	6·1
Brazil (Bahia)	5·15	5·2	5·3	5·2	5·5	5·7
Grenada	5·75	5·75	5·9	5·7	5·95	6·05
Samoa	6·15	6·2	6·3	6·5	7·05	7·15
Trinidad	5·65	5·65	5·75	5·8	6·5	6·3
Average ..	5·55		5·76		6·25	
SHELL						
West Coast of Africa (1) ..	18·5	—	18·7	—	18·9	—
(2) ..	17·0	17·0	17·0	17·3	19·35	19·25
Brazil (Bahia)	15·65	15·5	16·15	15·9	16·8	16·8
Grenada	15·25	—	15·6	15·4	16·1	16·3
Samoa	15·9	15·6	16·7	16·7	17·2	17·2
Trinidad	14·15	14·1	14·7	15·0	15·75	15·7
Average ..	15·85		16·3		17·2	

In Table IV my results are compared with those obtained by Miss D. M. Lowe; for nib the figures agree within 0·2 per cent., whilst for shell the maximum difference is 0·3 per cent.

The effect of roasting may cause up to 1 per cent. increase in the apparent fibre in nib and 2·3 per cent. in shell, and the calculation of shell is thereby rendered more difficult. The figures obtained with shell are generally lower than those recorded in Table III.

CALCULATION OF SHELL FROM FIBRE-CONTENT.—The calculation of shell from the fibre figure, or other determined factors, has received little attention in the literature, although it is obvious, from the Cocoa Powder Order and various legal actions which occasionally have been taken, that such computation is expected. Records covering the last twenty years show that various methods have been used to obtain the percentage of shell from the fibre figure. Some results have been calculated as the fat-free shell in the fat-free mixture, but this figure has sometimes been recorded wrongly as the shell on the original material. Other methods of calculation have considered the fat percentage and, occasionally, fat and moisture. In no instance has the fat and moisture in shell been considered.

In the calculation of shell it is necessary to take fully into consideration the fat and moisture, as it is self-evident that de-fatting and drying cause a great increase in the amount of shell apparently present. On the other hand, by calculating back to the original material, *i.e.* allowing for fat and moisture contents, conflicting results are liable to be obtained in certain instances. For example, suppose a cocoa (A) having a fat-content of 30 per cent. and a highly-pressed cocoa material (B) with fat-content 10 per cent. to show fibre figures, on the dry fat-free materials, of 6·3 for A and 6·2 for B. By the use of the arbitrary standards—5·8 and 18·5 per cent. for nib and shell respectively—calculation of the shell on the dry fat-free materials gives for A, 3·9 per cent., and for B, 3·2 per cent., but by working back to shell in the original nib mixture the figure for A becomes 1·8 and for B 1·4 per cent. If, however, the shell is calculated on A and B as received, the results are A, 2·7 and B, 2·8 per cent., which indicates incorrectly that cocoa A is purer, so far as shell is concerned, than the highly pressed material B. It is, therefore, misleading to record shell on the sample as received, and undoubtedly the fairest way, and certainly, from a manufacturer's point of view, the most useful way is to calculate back to commercially pure nib from which the cocoa has been prepared. In order to do this it is necessary to fix suitable standards for the average fat and moisture contents of roasted nib and shell, when the following equation can be applied:

If a = fat + moisture in roasted nib
b = fat + moisture in roasted shell
S = dry fat-free shell in the dry fat-free mixture calculated from the fibre figure according to:

$$S = \frac{100}{12{\cdot}7}\,(\text{fibre per cent.} - 5{\cdot}8)$$

then the roasted shell in the original nib mixture

$$= \frac{100\,S}{(100-S)\,\dfrac{(100-b)}{(100-a)} + S}\ \text{per cent.}$$

It has been found from a great number of tests that the sum of fat and moisture in roasted nib and shell averages 58 per cent. and 8 per cent. respectively, and, by substitution for *a* and *b*, the above equation becomes $\frac{84\ S}{184-S}$. This can again be expressed in terms of fibre on the dry fat-free material (F), when the following equation is established:

$$\text{Roasted shell in original nib mixture} = \frac{8400\ (F-5{\cdot}8)}{2337-100\ (F-5{\cdot}8)}$$

The following table has been drawn up from a graph based on this equation :

TABLE V

PERCENTAGE OF ROASTED SHELL IN ORIGINAL NIB MIXTURE CALCULATED FROM FIBRE PERCENTAGE

Fibre	Shell	Fibre	Shell	Fibre	Shell
5·8	0·0	7·4	6·2	11·0	24·0
5·9	0·3	7·5	6·6	11·5	27·0
6·0	0·7	7·6	7·0	12·0	30·2
6·1	1·1	7·7	7·4	12·5	33·8
6·2	1·4	7·8	7·8	13·0	37·4
6·3	1·8	7·9	8·3	13·5	41·3
6·4	2·2	8·0	8·7	14·0	45·5
6·5	2·5	8·1	9·1	14·5	49·9
6·6	2·9	8·2	9·6	15·0	54·4
6·7	3·3	8·3	10·0	15·5	59·5
6·8	3·7	8·4	10·5	16·0	65·0
6·9	4·1	8·5	11·0	16·5	70·9
7·0	4·5	9·0	13·2	17·0	77·3
7·1	4·9	9·5	15·7	17·5	84·5
7·2	5·3	10·0	18·3	18·0	91·7
7·3	5·7	10·5	21·1	18·5	100·0

In the scheme given for the calculation of shell in roasted nib four arbitrary standards had to be chosen, namely, fibre in dry fat-free nib and shell, and the sum of fat and moisture in roasted nib and shell. The latter were taken at 58 and 8, respectively, and calculation shows that variations of ± 1 per cent. would make a deviation of up to 0·3 per cent. on nib containing less than 5 per cent. of shell. Variations in the standards of 5·8 and 18·5 per cent. are more serious, but between the limits of 5·6 to 6·0 per cent. for nib and of 18·0 to 19·0 per cent. for shell, it can be shown that for amounts up to 5 per cent. of shell an accuracy of ± 1 per cent. should be obtained. Reference to Table III shows that the above figures do not by any means cover the ranges found, but, as it is customary for manufacturers to blend beans from various sources, and since slightly more than half the world's cacao is grown on the West Coast of Africa, the selected variants should cover most of the commercially prepared cocoas.

To ascertain how far the method was practicable, a number of roasted bean samples were shelled by hand, and known quantities of shell were added to known weights of ground nib. The mixture was then de-fatted, sieved and dried as described in the analytical method. With Bahia, Grenada and No. 7 (Table VI) the samples were prepared in two ways: first by adding coarse shell to the nib and grinding them together, and secondly by adding ground and sieved shell to the well-ground nib. This precaution was taken, as it was feared that some of the particles of shell might be left in the mortar, on the scrapers, etc., but no differences were found in the fibre figures. Sieved shell was added to the remainder of the samples, as this was considered a more satisfactory way of ensuring that the required percentage had been included. As an additional precaution the fibre percentages were determined by another chemist (Mr. W. T. Lunt), who followed the written process without other information, and his results, which are included in Table VI, show a high degree of concordance with mine.

TABLE VI

Source of beans	Degree of roasting	Intended for	Shell, on beans Per Cent.	Shell added Per Cent.	Fibre H.C.L. Per Cent.	Shell (from Table V) Per Cent.	Fibre W.T.L. Per Cent.	Shell (from Table V) Per Cent.
(1) West Coast ..	Normal	Cocoa	10·4	10·4	8·4	10·5	—	—
			—	—	8·3	10·0	—	—
(2) West Coast.. ..	,,	,,	11·1	2·0	6·45	2·3	6·4	2·2
(3) West Coast.. ..	,,	,,	11·0	2·5	6·55	2·7	6·5	2·5
(4) West Coast.. ..	Low	Chocolate	11·0	1·5	6·05	0·9	6·1	1·1
			—	—	—	—	6·1	1·1
(5) Grenada	High	,,	—	3·0	6·8	3·7	—	—
(duplicate preparation)	,,	,,	—	3·0	6·8	3·7	6·85	3·9
(6) Bahia	Low	,,	12·3	2·0	5·65	—	—	—
(duplicate preparation)	,,	,,	12·3	2·0	5·6	—	5·7	—
(7) Second quality ..	Very	Butter	11·0	2·0	5·85	0·2	—	—
	low	extrusion	—	—	5·9	0·3	—	—
(duplicate preparation) ,,	,,	,,	11·0	2·0	5·9	0·3	5·9	0·3

Examination of Table VI shows that satisfactory results are obtained with West Coast beans which have received normal roasting, and moderately satisfactory results with low-roasted beans intended for chocolate manufacture. Owing to the small size of Grenada beans, a higher roast is necessary before kibbling, and this tends to enhance the fibre figure, but even then the results can be considered fairly good. For Bahia beans it appears necessary to use a different standard for fibre on pure nib; this is of the order of 5·2 per cent. Beans intended for maximum butter extrusion, and consequently given a very low roast, should also be considered in a separate category and, tentatively, a standard of 5·4 per cent. for pure nib is recommended. It must be borne in mind, however, that the method is intended for the examination of cocoa powders on the assumption that these are prepared from beans containing at least a high proportion from the West Coast of Africa and that they have received normal roasting. Tests 6 and 7 in Table VI were chosen as being very abnormal, and therefore must be considered as special cases.

SUMMARY.—The method for the determination of crude fibre has been carefully examined with a view to making the process more accurate. The points investigated include: preparation of sample, type of apparatus, weighing and measuring, prevention of frothing, most suitable types of filters, treatment with alkali, and collecting and washing the crude fibre. Based on the findings, an analytical process is described capable of giving accurate duplicate determinations by the same or different operators. The process has been applied to fibre determinations on West Coast beans, and the tests include the effect of particle size, alkali treatment of mass (Dutch process), preparation of pressed cake, etc. A table of results is given showing the variation likely to be experienced when dealing with beans grown in different countries, and the effect of roasting has also been studied.

The calculation of cacao shell from the fibre figure has been considered in detail and recommendations are made that all computations should be based on the shell in the nib mixture, *i.e.* the purity of the nib from which the product is made should be used as the basis for comparison with other results. A table has been prepared based on certain arbitrary standards for fat and moisture in nib and shell, and the effect of variations in these arbitrary standards has been considered.

A number of known mixtures have been examined, with satisfactory results in five instances out of seven, while the two unsatisfactory ones are shown to be due to the type of bean and the extremely low roasting given. The determinations were repeated by another chemist and excellent agreement was obtained. Although the method is not yet of universal application it has definite value when used in a manufacturer's own laboratory.

In conclusion, acknowledgment is made to the late Mr. A. W. Knapp and to Mr. J. R. Johnson for their continued interest and advice, and to Messrs. Cadbury Bros., Ltd., for permission to publish this investigation, which was carried out in their laboratories at Bournville.

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The Analysis of Malt Extract by Selective Fermentation

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A METHOD for the analysis of malt extract and similar mixtures of carbohydrates has been published by McLachlan,[1] who gives references to earlier work. As McLachlan's method, with slight modifications, has proved very satisfactory in this laboratory, a description is given of the modified method. Some observations on the carbohydrates present in malt extract, particularly the unfermentable fraction, are also added. It may perhaps be emphasised that the data here given refer wholly to diastatic extracts, and the composition of some non-diastatic extracts may be somewhat different.

Essentially the method consists in comparing (*a*) an unfermented portion of a solution of the material to be analysed, (*b*) another portion of the same solution after fermentation with a yeast known to ferment dextrose but not maltose, and (*c*) a further portion after fermentation with a maltose-fermenting yeast. As dextrose-fermenting yeasts ferment also laevulose (as well as mannose, if present), the difference between (*a*) and (*b*) gives a measure of these monosaccharides, and as maltose-fermenting yeasts also ferment the above monosaccharides the difference between (*b*) and (*c*) gives a measure of the maltose content. McLachlan, following Nanji and Beasley,[2] used both Saaz and Frohberg yeasts and reported the difference between the results obtained with these as "other fermentable sugars."

PREPARATION OF SOLUTION.—The method preferred is to weigh out 120 to 150 g. of extract and wash it into a large flask with about 800 ml. of nearly boiling distilled water,[4] boil for at least ten minutes, cool to room temperature, make up to a litre and filter. Results of the analysis may conveniently be expressed as percentages of hot-water-soluble solids. The insoluble residue, though bulky when wet, averages only about 0·6 per cent. of the total solids, and for routine purposes the percentage of insoluble substances may be assumed to be constant, and results are then readily convertible to percentages of total solids.

One hundred ml. of the solution, measured at 15° C., is transferred to each of three or more sterile 300-ml. round flat-bottomed flasks, plugged with cotton-wool, and the solution is boiled in the flasks for a few minutes and cooled.

INOCULATION AND INCUBATION.—If the solution is sterilised in the flasks as described, a very small inoculation is sufficient. It is enough to dip a sterile wire loop once or twice into a culture of the yeast—preferably an active culture in malt extract solution—and then into the solution under test. The flasks (including at least one not inoculated) are incubated at 20° to 21° C. for nine days, the contents being gently swirled on the third and sixth days. When 100 ml. of solution in a 300-ml. flask are used, the solution has a large surface, so that aeration is sufficient and fermentation is rapid. The standard time of nine days adopted has always proved ample and has on occasions been shortened by one or two days without appreciably affecting the results. McLachlan describes the fermentation as being complete in three weeks and "usually in a fortnight." The difference is possibly due to his having used deep layers in tubes. The uninoculated flask usually develops a slight deposit, probably due to oxidation, but should show no sign of fermentation and develop no turbidity or acid odour.

CHOICE OF YEASTS.—For the yeast fermenting dextrose but not maltose McLachlan recommends *Saccharomyces exiguus*. The yeast obtained under this name from the National Collection of Type Cultures did not appear to ferment maltose, but it gave a heavy mycoderma-like skin on the surface of the solution, and the fermented liquid was difficult to filter and very acid. This strain was therefore not used. A yeast isolated in this laboratory (originally from a sample of fermented tomato sauce) and known here as "Yeast No. 4" has, however, proved completely suitable.* It has no effect on maltose but ferments dextrose and laevulose vigorously and is satisfactorily clarified.

As regards the maltose-fermenting yeast it has been found (see Table II) that there is no appreciable difference, in respect of carbohydrate fermented, between Saaz and Frohberg yeasts, as supplied by the National Collection of Type Cultures, or between either of these and any of a number of other strains tried. Probably any ordinary brewer's yeast that gave satisfactory clarification would be found suitable.

EXAMINATION OF THE SOLUTIONS.—It is considered preferable to get rid of most of the yeast before heating the solutions. If suitable strains of yeast have been used, this is readily accomplished by filtration through an ordinary small filter-paper and the yeast can be washed on the paper once or twice with a gentle stream of water without producing more than a faint turbidity in the filtrate. The filtrate and washings are evaporated on the water-bath to about 50 ml., cooled, and made up to 100 ml. at 15° C. For the examination of the de-alcoholised solution several methods have been tried.

(*a*) *Total Solids calculated from Density of Solution.*—There are several obvious sources of error, particularly those arising from the facts that (i) there is uncertainty as to the "solution divisor" to be used, and the correct divisor for the residual solids after fermentation of maltose is almost certainly different from that for the original total solids, and (ii) other substances besides the fermented carbohydrate are removed by the yeast, and probably some non-volatile substances are formed.

Nevertheless this simple and rapid method is accurate enough for many purposes in routine testing. Different strains of yeast were found to give slightly different results. The figures quoted below have been obtained by using throughout the divisor 3·90, densities being measured by means of the specific gravity bottle at 15° C.

(*b*) *Reducing Sugar by Fehling's and similar Methods.*—This is the method that I consider the most satisfactory. All results quoted below have been obtained by the volumetric method of Lane and Eynon.[3] As a mixture of sugars is dealt with, the results are worked out as follows:—The reducing sugar in the unfermented solution is expressed as dextrose, that left in the solution fermented by the dextrose-fermenting yeast is also expressed as dextrose, and the difference is taken as dextrose fermented. The sugar left by the dextrose-fermenting yeast is now re-calculated as maltose, and the sugar left by the maltose-fermenting yeast is also expressed as maltose, and the difference is taken as maltose fermented. Clarification of the solutions by lead acetate before titration has not been found necessary. The clarification can, however, be carried out if desired and does not measurably affect the results.

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* This strain has been lodged with the National Collection of Type Cultures.

(*c*) *Optical Rotation.*—It was found by McLachlan (*loc. cit.*) that the sugars in malt extract fermented by a dextrose-fermenting yeast have a low rotation, and probably consist largely of laevulose. The rotation of this fraction is, moreover, somewhat variable, and hence cannot be used as a measure of the sugar removed by the dextrose-fermenting yeast. My experience confirms this. For the maltose fraction the rotation difference is, with some samples of extract, slightly lower than would be expected if the fraction consisted of maltose alone. In any event the rotation measured is small and therefore subject to error.

The figures given below have been obtained after decolorising with phosphotungstic acid and are calculated on the anhydrous sugar deduced as in the method given above. For routine purposes the rotation figure is regarded as an approximate check only.

(*d*) *Total Sugar, estimated as Dextrose after Acid Hydrolysis.*—Hydrolysis was effected by heating with 5 per cent. sulphuric acid on the water-bath for four hours, and the solution was left overnight before being neutralised and titrated by Lane and Eynon's method.

Results are in fair agreement with those obtained by direct titration of reducing sugars and afford some confirmation of the assumption that the dextrose and maltose fractions consist essentially of monosaccharide and disaccharide respectively. For routine purposes the estimation of these fractions by the hydrolytic method offers no special advantage and is probably less accurate than direct titration, but it is considered to be the best method available for the determination of unfermentable carbohydrate, *i.e.* that not fermented by the maltose-fermenting yeast. Hence this procedure is usually applied to the one solution only (*vide infra*).

TABLE I

Result of examination of solution containing 2·00 *g. of dextrose and* 3·65 *g. of anhydrous maltose per* 100 *ml., in yeast water*

(Results expressed as grammes per 100 ml. of solution)

Result obtained from	Dextrose fraction (Difference between solution unfermented and fermented by "yeast 4")	Maltose fraction (Difference between solutions fermented by "yeast 4" and by a strain of *Sacch. ellipsoideus*)
1. Density	1·87	3·64
2. Titration of reducing sugar	1·95	3·60
3. Titration of total sugar after acid hydrolysis ..	1·80	(dextrose × 0·95) 3·45
4. $[\alpha]_D$ for fermented sugar	56°	142°

TESTS ON SYNTHETIC MIXTURES.—Table I gives a typical set of results obtained on a synthetic mixture and indicates the degree of accuracy to be expected when operating on an unknown mixture. The sugars were dissolved in yeast-water and the mixture was treated by the methods given above for malt extract solution. In such mixtures the amount of carbohydrate left unfermented by the maltose-fermenting yeast is too small for accurate determination by titration, but is found by gravimetric methods to be of the order of 0·05 per cent., calculated as maltose, and this figure has been taken in calculating the maltose fermented. After the action of the maltose-fermenting yeast, the solution, clarified by means of phosphotungstic acid, has a rotation about 0·07°.

TABLE II

Maltose fraction of malt extract fermented by various yeasts. (Difference between solutions fermented by "Yeast 4" and by yeast named)

(Results expressed as percentage of total soluble solids in original extract)

Results obtained from	Frohberg yeast	Saaz yeast	*Sacch. ellipsoideus* var. *cratericus*	"Yeast 2"	Local brewery yeast
1. Density	43·5	45·6	43·8	44·9	45·5
2. Titration of reducing sugar	44·3	44·6	44·4	44·2	44·6
3. Titration of total sugar after acid hydrolysis (dextrose × 0·95) ..	41·6	42·1	42·1	40·0	41·4
4. $[\alpha]_D$ for fermented sugar on figure 2 above	119°	122°	115°	115°	125°

NOTE. Yeasts in the first three columns are National Collection of Type Culture strains. "Yeast 2" is a non-sporulating wild yeast isolated from local sources.

THE UNFERMENTABLE CARBOHYDRATES OF MALT EXTRACT.—It seems to have been generally assumed that the unfermentable carbohydrates of malt extract consist of dextrins. These might be either "stable dextrin" or bodies of the malto-dextrin type or both. McLachlan reported the unfermented carbohydrate as "dextrins," deducing the quantity from the optical rotation after fermentation, on the assumption that the dextrin present has $[\alpha]_D = +180°$.

With regard to the possible presence of malto-dextrins, McLachlan comments that "the method given in the *Chemists' Year Book*, in which fresh malt-extract is used to hydrolyse malto-dextrin, was tried and found unsatisfactory." The method referred to, which is practically that of Morris and Moritz, has been applied in this laboratory to a number of samples of diastatic malt extract and also to brewer's worts, and it has been found that, whereas the worts contain varying proportions of malto-dextrin, none has ever been found in the malt extracts. No sample of diastatic malt extract that we have examined has ever shown a measurable increase in reducing power on treatment with malt diastase, whether the treatment was carried out before or after removal of the fermentable sugars. It would appear, therefore, that during the preparation of the extract any malto-dextrins originally present are hydrolysed.

Figures for the unfermentable fraction of a typical sample of diastatic malt extract are given in Table III on page 107.

TABLE III

Characters of unfermentable matter of a diastatic malt extract

(Expressed as percentages of total solids of the original extract)

	Total unfermentable matter	Unfermentable matter soluble in 90 per cent. alcohol	Unfermentable matter insoluble in 90 per cent. alcohol
1. Total solids	37·4	7·2	27·7
2. Reducing sugar calculated as maltose	12·9	3·5	9·7
3. Total sugar by acid hydrolysis, calculated as:			
(*a*) Dextrose	20·8	3·7	16·1
(*b*) Dextrin (dextrose × 0·90)	18·7	3·3	14·5
4. $[\alpha]_D$	24·2°	6·3°	20·0°
5. R value (relative reducing power, maltose = 100), from 2 and 3(*b*)	69	112	67
6. $[\alpha]_D$, for sugar calculated as dextrin, from 3(*b*) and 4	128°	52°	131°

Stable dextrin is insoluble in 90 per cent. alcohol and has, according to Ling and Nanji,[4] $[\alpha]_D = 185°$, $R = 14$. From the figures of Table III it is clear that of the unfermentable substances responsible for the residual rotatory and reducing power, a fraction of the order of a fifth (the alcohol-soluble fraction) is definitely not dextrin, while the balance certainly does not consist wholly of dextrin.

In the Morris–Moritz method stable dextrin is determined by fermenting with yeast in the presence of diastase, under which conditions the dextrin is said to be fermentable. As the diastase solutions are apt to contain acid-forming bacteria and cannot be boiled for sterilisation, the process is, in my experience, a somewhat uncertain one. Under favourable conditions, however, the fermentation will proceed satisfactorily. In the presence of the diastase the total unfermentable matter of malt extract is reduced a little, but neither the reducing power nor the rotation of the residue is appreciably lowered. This is in contrast with the residual carbohydrate of unevaporated worts, which in presence of diastase is fermented away to very low concentrations.

The unfermentable sugars of malt extracts, when heated on the water-bath for about an hour with phenylhydrazine reagent, yield a small quantity of glucosazone, but no other osazone could be found. Lead acetate precipitated none of the reducing substance and lead subacetate only a small proportion. No satisfactory separation of the carbohydrates from the other unfermentable matters has yet been effected, and the nature of the unfermentable carbohydrates has not been further investigated. It is considered that there is no justification for regarding them as dextrins, and they are probably largely hexosans produced during the evaporation.

For purposes of routine analysis it is my practice to hydrolyse the residue from the maltose fermentation, and determine the reducing sugar as dextrose by titration. This figure, multiplied by 0·90 (as if correcting to dextrin, but the figure is an arbitrary one in the circumstances), is returned as "unfermentable carbohydrates."

OTHER SUBSTANCES.—All samples of malt extract examined contained a considerable proportion of substances other than fermentable sugars or substances hydrolysable by acid to reducing sugars. After deducting mineral matter and protein (N × 6·25) the "other substances" are usually about 10 to 15 per cent. of the total solids. Most of these substances are precipitated by alcohol as a dark-coloured gummy mass. In some of the older methods of analysis, *e.g.* that given by Parry,[5] this would be returned as "dextrin," which is clearly incorrect.

Some typical analyses are given below (Table IV).

TABLE IV

Analysis of diastatic malt extracts

(Results expressed as percentage of total hot-water-soluble solids)

	A typical New Zealand-made extract Per Cent.	Well-known brand of British extract Per Cent.	Hot-water-soluble extract from a sample of malt extract with cod-liver oil Per Cent.
Dextrose and laevulose	16·6	18·0	18·9
Maltose	44·5	40·0	42·5
Unfermentable carbohydrates	18·7	20·1	18·0
Protein (N × 6·25)	6·5	8·2	20·6
Ash	2·1	1·8	
Other substances, by difference	11·6	11·9	
$[\alpha]_D$ of dextrose fraction	+22°	+19°	+34°
$[\alpha]_D$ of maltose fraction	+125°	+140°	+139°

SUMMARY.—(1) A modification of McLachlan's method for the analysis of malt extract by selective fermentation is recommended.

(2) A yeast that I have isolated is recommended for fermenting glucose and laevulose in the presence of maltose.

(3) Several maltose-fermenting yeasts, including the National Collection of Type Cultures strains of Saaz and Frohberg yeasts, show no difference in their action on the carbohydrates of diastatic malt extracts.

(4) Diastatic malt extracts contain no maltodextrins; the unfermentable carbohydrates include substances other than dextrins, and possibly no true dextrin is present. It is suggested that the unfermentable sugars are largely hexosans produced during evaporation.

Acknowledgment is made to the Wilson Malt Extract Co., Ltd., to Kempthorne Prosser & Co., Ltd., and to New Zealand Breweries, Ltd., all of whom have supplied material for analysis.

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The Electrolytic Separation of Cobalt from Nickel by Deposition as Cobaltic Oxide

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OWING to the great physical and chemical similarity between cobalt and nickel a satisfactory method of electrolytic separation has not hitherto been devised. Balachowsky[1] has described a method of separation in which the nickel is deposited alone from an ammonium acetate solution in the presence of ammonium thiocyanate and urea, cobalt being held up, but the method is extremely complicated and the results insufficiently accurate. Coehn and Gläser[2] utilised the fact that cobalt can be deposited from a faintly acid solution in the form of cobaltic oxide, Co_2O_3, as a means of separating cobalt and nickel. Cobalt, unlike nickel, but like lead, bismuth, silver and manganese, deposits both as metal on the cathode and as oxide on the anode. In order to obtain the oxide completely, it is necessary to prevent the deposition of the metal. Coehn and Gläser attained this by the addition of potassium dichromate as a depolariser and by careful adjustment of the current to such a value that hydrogen was not liberated at the cathode. Under such conditions the rate of deposition of cobaltic oxide is, however, extremely low, 0·08 g. of the oxide being deposited in rather more than 20 hours, and the separation is too tedious to be of much practical importance.

In the method described below, the Sand revolving-diaphragm electrode[3,4] was used to separate the cathode from the cobalt solution, thus inhibiting the deposition of cobalt as metal. Cobaltic oxide is not deposited from a solution with acidity much stronger than *p*H 3·5, and as by screening the cathode the anolytic solution becomes more strongly acid with the progress of the electrolysis, it was found necessary to buffer the anolyte with sodium acetate.

DEPOSITION OF COBALT AS COBALTIC OXIDE.—A standard cobalt solution containing approximately 0·01 g. of cobalt per 10 ml. was prepared by dissolving cobalt sulphate (AnalaR) in water. An aliquot portion of this solution was acidified by the addition of 1 ml. of glacial acetic acid and buffered to a *p*H of about 5 by the addition of 10 g. of sodium acetate. The solution was diluted to about 100 ml. and electrolysed, the Sand revolving-diaphragm electrode being used as cathode and a platinum gauze electrode as anode; the cobalt solution was the anolyte, and a 2 *N* nitric acid solution the catholyte. The electrolysis was carried out at a temperature of 90°–95° C., beginning with a current of 0·5 amp. This was raised, after 10 minutes, to 1·0 amp., and the catholyte was flushed into the anolyte by the addition, to the catholyte, of about 5 ml. of 2 *N* nitric acid. The deposition was continued for a further 20 minutes, the catholyte being once more flushed out after 10 minutes. Under these conditions a firm adherent deposit of cobaltic oxide was obtained. The deposit was weighed and dissolved by warming the electrode with 20 ml. of 20 per cent. sulphuric acid, 2 drops of sulphurous acid solution being added to facilitate solution and excess of sulphur dioxide boiled off. The solution was neutralised with ammonia, and 20 ml. of ammonia (sp.gr. 0·880) were added in excess. The mixture was diluted to about 150 ml. and cobalt was deposited as metal by electrolysing between standard Sand electrodes,[5] for 20 minutes at room temperature, with a current of 3 amps. The results obtained with varying amounts of cobalt are given in Table I. Cobaltic oxide, unlike lead peroxide, does not absorb moisture, and the theoretical factor of 0·71 may be applied for converting the weight of cobaltic oxide into the equivalent weight of cobalt.

TABLE I

Cobalt taken g.	Equivalent as cobaltic oxide g.	Cobaltic oxide deposited g.	Cobalt deposited g.
0·0098	0·0138	0·0140	0·0099
0·0098	0·0138	0·0141	0·0098
0·0197	0·0277	0·0279	0·0201
0·0197	0·0277	0·0279	0·0199
0·0394	0·0556	0·0560	0·0397
0·0394	0·0556	0·0560	0·0398
0·0394	0·0556	0·0559	0·0397

(It was not found possible to obtain an adherent deposit of cobaltic oxide with amounts much above these weights.)

SEPARATION OF COBALT FROM NICKEL.—Two to three g. of nickel sulphate were added to a portion of the standard cobalt solution, and the mixture was buffered and electrolysed as described above. It was observed that the deposited cobaltic oxide contained a little nickel, this being in accordance with the findings of Coehn and Gläser (*op. cit.*).[2] It was therefore necessary to dissolve the oxide and make a second separation. The presence of excess of mineral acid had previously been found to prevent complete deposition of cobaltic oxide, and the following procedure was adopted:—The oxide was dissolved by warming the electrode with 20 ml. of 2 *N* nitric acid with the addition of two drops of sulphurous acid solution, and evaporating the nitrate solution to dryness, the last stages being carried out in an evaporating basin over a water-bath, to prevent overheating of the nitrate. This was then taken up in water, and the solution was buffered and electrolysed as before. The deposit of cobaltic oxide thus obtained was free from nickel. Results are given in Table II.

TABLE II

Cobalt taken g.	Equivalent as cobaltic oxide g.	Cobaltic oxide deposited g.	Equivalent as cobalt g.
0·0120	0·0169	0·0168	0·0119
0·0120	0·0169	0·0169	0·0120
0·0240	0·0338	0·0336	0·0239
0·0240	0·0338	0·0336	0·0239
0·0360	0·0507	0·0508	0·0361
0·0360	0·0507	0·0508	0·0361
0·0480	0·0676	0·0678	0·0481
0·0480	0·0676	0·0675	0·0479

DETERMINATION OF COBALT AND NICKEL.—In the electrolytic analysis of nickel alloys previously described[6] any cobalt present would be deposited together with nickel, and the method worked out above was adapted for analysis of nickel alloys containing cobalt.

The conditions for such determinations were simulated by taking a solution containing a known amount of cobalt and nickel. Two g. of sodium sulphite, 10 g. of ammonium sulphate and 20 ml. of ammonia (sp.gr. 0·880) were added to the solution, which was diluted to 150 ml. and electrolysed for 20 minutes, at 70° C., with an auxiliary potential of 1·0 volt to a saturated calomel auxiliary electrode.[7] Cobalt and nickel were deposited together. The deposit was weighed and dissolved in 20 ml. of 20 per cent. nitric acid. The solution was evaporated to dryness, and the mixed nitrates taken up in water, and the cobalt deposited as oxide as described above. The weight of cobaltic oxide was calculated to the equivalent weight of cobalt, and the amount of nickel determined by difference. Results are given in Table III.

TABLE III

Cobalt taken g.	Nickel taken g.	Cobalt and nickel deposited g.	Cobaltic oxide deposited g.	Equivalent as cobalt g.	Nickel by difference g.
0·0120	0·1240	0·1360	0·0170	0·0121	0·1239
0·0060	0·2480	0·2542	0·0085	0·0060	0·2483
0·0240	0·2480	0·2724	0·0340	0·0241	0·2483
0·0060	0·9920	0·9983	0·0084	0·0059	0·9924

I wish to thank Dr. H. J. S. Sand for his interest and assistance.

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THE SIR JOHN CASS TECHNICAL INSTITUTE
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Errata.—VITAMIN A AND VITAMIN D CONTENTS OF BUTTER (January issue).

P. 22, l. 14, *for* M ± 6 *read* M ± σ.
,, l. 24, *for* 2 × P.E. *read* 3 × P.E.
,, l. 25, *for* 2·576 *read* 3·864

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE TITRATION OF IODIDE IN PRESENCE OF CHLORIDE WITH SILVER NITRATE, USING ROSE BENGAL AS ADSORPTION INDICATOR

FAJANS and Wolff (*Z. anorg. Chem.*, 1924, **137**, 233) first studied the determination of iodide in the presence of chloride by titration with silver nitrate, using certain substituted fluoresceins, including Rose Bengal (dichloro-tetraiodofluorescein), as adsorption indicators. They found that the results for iodide thus determined were slightly high. The excess of silver nitrate required when chloride was present depended on the relative proportions of the iodide and chloride in the solution, the extreme limits of error being from 0·45 to 1 per cent. In a paper that I published (ANALYST, 1936, **61**, 315), it was stated (*loc. cit.*, p. 317) that "the colour change with Rose Bengal coincides strictly with the quantitative precipitation of silver iodide, and without any co-precipitation of silver chloride." This statement now requires to be qualified. I had the advantage of discussing this matter with Professor Fajans, who spent some weeks in Cambridge two years ago, and who very kindly came to see some determinations actually carried out. The titrations of Fajans and Wolff were carried out in conical flasks, and the liquid was gently swirled, the end-point of the reaction being observed by the change of colour in the mass of liquid. In my determinations the titrations were carried out in stoppered bottles which were violently shaken, and the end-point of the reaction was taken as that point at which the dyestuff was removed from the supernatant liquid and adsorbed on the precipitate. It will be seen in what follows, that when chloride is present, there is a slight, but decided, excess of silver nitrate required for quantitative reaction with the iodide as determined with the aid of Rose Bengal.

In order to decide the question as exactly as possible, weighed quantities of silver nitrate were taken for each experiment. A measured quantity of a standard solution of potassium iodide (15·347 g. per litre) was run from a Stas pipette, having a capacity of 63·73 ml., into the solution of silver nitrate. The quantity of silver nitrate that was weighed was always slightly less than that required for quantitative reaction with the potassium iodide. The reaction was then completed by adding a very dilute solution of silver nitrate (1·62 g. per litre), the end-point being determined with Rose Bengal. Flocculation was aided by the use of a few drops of a solution of lanthanum nitrate. Precisely parallel experiments were then carried out, in which approximately one-third of a molar proportion of potassium chloride was added to the standard solution of potassium iodide. It may be remarked that Fajans and Wolff (*loc. cit.*) found that the maximum error occurred when the molar ratio of chloride to iodide was between 0·1 and 0·5.

A number of determinations were carried out, and it should be noted that special experiments with the measuring vessels showed that the Stas pipette was reliable to one part in six thousand. The final titrations with dilute silver nitrate were accurate to ±0·25 ml. Taking the various factors into consideration, it was estimated that the maximum error in a determination would be of the order of one part in two thousand, and would certainly be less than one part in one thousand. AnalaR reagents were employed in all the determinations.

Silver nitrate weighed g.	Dilute silver nitrate required ml.	Potassium chloride	Ratio $\frac{AgNO_3}{KI}$ determined
0·9582	24·5	none	1·021
0·9694	17·0	,,	1·020
0·9992	1·75	present	1·024
0·9597	26·0	,,	1·024

From the few results which have been quoted—and it may be added that numerous other experiments gave identical results—it will be seen that when potassium chloride was present, the consumption of silver nitrate was slightly, but decidedly, greater, *viz.* from three to four parts per thousand, than when pure potassium iodide was titrated. The error was, however, materially lower than that observed by Fajans and Wolff.

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THE *m*-DINITROBENZENE REACTION OF OUABAIN AND ITS APPLICATION TO THE EXAMINATION OF EAST AFRICAN ARROW POISON

In a recent paper (Analyst, 1938, 63, 480) a reaction between *m*-dinitrobenzene and ouabain was described. This reaction, which is also given by digitoxin, digoxin and gitoxin (private communication from Dr. T. A. Henry), has now been modified to enable ouabain to be estimated with greater accuracy.

In the modified technique the solution, preferably in methyl alcohol, of the glycoside is measured into the bottom of a test-tube. This is placed in a boiling water-bath and the last traces of solvent are removed by attaching the warm tube to a vacuum pump. Care is taken to prevent loss by spurting and a small glass bead may be added. When cool, the residue is dissolved in exactly 1 ml. of 50 per cent. ethyl alcohol, 0·1 ml. of *m*-dinitrobenzene reagent is added, and the tube is placed in an ice-bath controlled at 0° C. After ten minutes 0·2 ml. of 20 per cent. sodium hydroxide solution is added, and the tube is left at 0° C. for exactly five minutes. The blue colour of the solution is rapidly measured in a 1-cm. tube in the B.D.H. Lovibond Colorimeter, some yellow units being necessary to produce a match. Final exact measurements may be made on a duplicate sample, since the blue colour fades. The amount of ouabain is read off from a curve prepared with pure ouabain (B.D.H.). The curve used in this laboratory is a straight line running from zero to 0·175 mg. of ouabain; 12·0 blue (about 1·4 yellow) units.

An attempt has been made to check colorimetric estimations of the strength of native arrow poison by a simplified modification of the physiological assay described in the B.P., 1932, using local frogs in groups of four. Some of the results obtained are given below:

Crystalline Ouabain

(Crystalline ouabain (B.D.H.) at about 27° C.)

No. of frogs in batch	Dose per g. of body wt. mg.	Result
4	0·0004	All died
4	0·0002	Two died
4	0·0001	All lived

MUSOMA ARROW POISON

(Colorimetric assay showed 16·2 per cent. of ouabain)

No. of frogs in batch	Dose per g. of frog mg.	Corresponding dose of ouabain (calculated colorimetric assay) mg.	Result
4	0·0022	0·00036	All died
4	0·00099–0·00117	0·00016–19	Two died
4	0·00062	0·0001	All lived

LIWALE ARROW POISON

(Colorimetric assay showed 10·2 per cent. of ouabain)

No. of frogs in batch	Dose per g. of frog mg.	Corresponding dose of ouabain mg.	Result
4	0·004	0·0004	All died
4	0·002	0·0002	One died
5	0·001	0·0001	All lived

In estimating strophanthin, if it is assumed that the hypothetical genin of ouabain is colorimetrically equivalent to strophanthin and twice as toxic and that 2·17 parts of strophanthidin K correspond to 1·0 parts of strophanthin, the amount of ouabain estimated colorimetrically in an extract from strophanthus should be multiplied by the factor 0·64. A tincture of strophanthus B.P. was diluted tenfold with methyl alcohol, and 0·1 ml. of the diluted tincture showed 4·2 and 4·1 Lovibond blue units corresponding to 0·63 per cent. of ouabain colorimetrically, or 0·41 per cent. of ouabain, when converted by the factor 0·64. The B.P., 1932, specifies the physiological equivalent of 0·42 per cent. of crystalline ouabain.

SINGIDA ARROW POISON

Histological and chemical examination showed that the poison was derived from *Strophanthus eminii* seeds, and contained the colorimetric equivalent of 4·64 per cent. of ouabain (physiologically equivalent to 3·0 per cent. of ouabain).

No. of frogs in batch	Dose per g. of frog mg.	Physiological equivalent of ouabain mg.	Result
4	0·03	0·0009	All died
4	0·015	0·00045	All died
4	0·0075	0·0002	All lived

These results suggest that the method is worth further study as a possible method for the colorimetric assay of tincture of *Strophanthus*, a standard tincture being used for reference.

The reaction has been found to be much more selective than was originally supposed. Under the conditions described above benzaldehyde, acetaldehyde, formaldehyde, ethyl acetoacetic ester, camphor (0·1 ml. or 0·1 g.) give only slight colours. Acetone and diacetone alcohol (0·1 ml.) give a reddish-violet colour, easily distinguished from the deep blue of ouabain. Attention should be drawn to the somewhat similar colours obtained with androsterone and related compounds, but under different conditions (*Biochem. J.*, 1938, **32**, **1312**).

A colour reaction with ouabain is given not only by dinitrobenzene but by other *m*-dinitro compounds (picryl chloride, 1-chloro-2 : 4-dinitrobenzene, and 2 : 4-dinitro-aniline, but not by 2 : 4-dinitro-toluene), and the previously described reaction with picric acid appears to be part of this general reactivity of the *m*-dinitro compounds. Of all the compounds examined, *m*-dinitrobenzene appears the most suitable. In this connection reference may be made to the general reaction of the *m*-dinitro compounds with cyanides, leading to the formation of *m*-purpuric acid (Feigl, *Qual. Anal. mit Hilfe von Tüpfelreaktionen*, 3rd Ed., p. 382).

East African arrow poisons have been described as prepared from the root and bark of *Acocanthera* (A. Stoll, *The Cardiac Glycosides*, p. 17). From the results of the histological examination of a large number of Tanganyika arrow poisons there are no grounds for supposing that bark, except in so far as it forms part of the stem and root, is used as raw material for the preparation of arrow poison. The following results were obtained in a colorimetric assay of the various parts of *Acocanthera*.

	Ouabain Per cent. by weight
Acocanthera longiflora fruit pulp, dried	trace, less than 0·05
,, ,, seeds	5·4
,, ,, flowers..	0·9
,, ,, wood ex young stem	0·7
,, ,, bark ex young stem..	trace
,, ,, leaves	0·4
Acocanthera venenata (woody portions used in arrow poison manufactured at Liwale)	1·1
Acocanthera sp., roots (ex British Somaliland)	3·0

The crystals obtained from the seeds of *Acocanthera* give all the colour reactions of ouabain, but are contaminated with a foreign substance and have not been obtained in a pure state. Similar difficulty has been experienced in obtaining pure material from Musoma arrow poison, although the crystalline form and colour reactions of the material isolated resemble those of ouabain.

Poison recrystallised materials from Liwale gave the following results:
Dried at 115° C. in a high vacuum.
Found: C, 59·19; H, 7·46 per cent.
C, 59·13; H, 7·56 per cent. (micro-analyses, Dr. G. Weiler).
$C_{29}H_{44}O_{12}$ (calculated C, 59·56; H, 7·58 per cent.).
Micro-polarimeter: $[\alpha]^{D}_{25} = -28^\circ$ (approximate) calculated to anhydrous ouabain.
Hepta-acetyl-anhydro-ouabain prepared, m.p. 282° C., micro-crystalline characters as described in ANALYST, 1938, **63**, 481.

The colorimetric assay of all *Acocanthera* and poison material, but not that of *Tinct. Strophanthi*, was carried out on extracts cleared with basic lead acetate, excess of lead being subsequently removed by means of hydrogen sulphide.

From the histological, physiological and chemical examinations of Tanganyika arrow poison carried out during the past four years it is concluded that the common arrow poison of the territory is prepared from the woody portions of *Acocanthera*, and that the active principle is mainly ouabain. The Tindiga tribe prepare their poison from the seeds of *Strophanthus eminii*, and in the Ufipa area poison is prepared from a species of *Urginea* (akin to *Urginea sanguinea* Schinz). No example of a poison prepared entirely from a species of *Adenium* has been encountered. These findings are confirmed by information from native sources kindly collected by officials in the Service. I thank the Director of Medical Services for permission to publish this note. W. D. RAYMOND

MEDICAL LABORATORY
DAR ES SALAAM

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SALE OF "SAL VOLATILE"

On December 9th a druggist was summoned at the Thames Police Court by the Stepney Borough Council for selling, to the prejudice of the purchaser, sal volatile deficient in alcohol to the extent of 95·4 per cent.

The inspector, giving evidence, said that he asked for a bottle of sal volatile, and that the man in the shop handed him a small bottle labelled "Sal volatile N.F.," for which he paid 1s.

Mr. D. Henville, Public Analyst to the Borough of Stepney, said that, strictly speaking, sal volatile was spirit of sal volatile, but no one ever used the full term. Everyone called it sal volatile, and all samples in Stepney under the Food and Drugs Act were taken in that name. Liquor Ammon. Aromat. contained only about 3 per cent. of alcohol, whilst sal volatile contained 65 to 70 per cent., which made a considerable difference in the price.

The defendant said that he had never heard of sal volatile. It was not in the British Pharmacopoeia; spirit of sal volatile was not allowed in any formula under the National Health Insurance. The inspector had asked for two ounces of sal volatile, and as he had stated that the case was an emergency one, he had been supplied with a bottle labelled "Sal volatile, National Health Insurance Formula."

The Magistrate (Mr. Everard Dickson) asked why the bottle obtained with the official sample had not been labelled "Liquor Ammon. Aromat.," instead of having the letters "N.F.," and pointed out that average members of the public did not know what those letters meant, although they knew the meaning of sal volatile. He was bound to say that the case gave him considerable difficulty, but the fact emerged that sal volatile was asked for, and what was provided was a mixture of sal volatile without the addition of alcohol. As the difference was represented in terms of value, he must arrive at the conclusion that there was a sale to the prejudice of the purchaser, but he did not regard it as a serious case.

The summons was dismissed under the Probation of Offenders Act on payment of £2 2s. costs.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND DISTRICT OF AMSTERDAM (HOLLAND)

Report of the Public Analyst for 1937*

In this district, with a population of 994,760, the number of articles of foodstuffs inspected in shops and markets was 493,716, and 33,705 samples were taken by the inspectors for analysis in the Laboratory. Of 20,276 samples of milk, 188 were condemned on account of added water, 660 for deficiency in fat, and 735 because of low reductase numbers. Of 2079 samples of bottled pasteurised milk, 128 were condemned on account of a high count of bacteria (more than 25,000 per ml.), or because of the presence of *B. coli*. The bad samples were taken from small old plants in which the milk was heated and cooled in the bottle. For infringements of the Milk Regulations 123 sellers were fined. Of 794 samples of ice-cream, 380 were condemned for a high count of bacteria (more than 100,000 per ml.) or because of the presence of *B. coli*. Several small-scale producers were prosecuted.

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* The interest taken in the work of the Amsterdam food control service (Keuringsdienst van Waren) by a party of English food chemists, when visiting the Institute in 1936, induced the Director to send us these notes. (*Cf.* Analyst, 1932, 57, 15.)

Inspections of bakeries were made on 5265 occasions, and underweight loaves were found on 750 of these visits; prosecutions were instituted in 171 cases and fines were inflicted.

Wines were analysed in the Laboratory and tasted by experts. Of 183 samples, 45 were condemned, as not in accordance with the label under which they were sold.

Sausages were frequently found to contain more than the allowed percentage of starch (4 per cent.) or to contain artificial colouring matter (124 of 563 samples).

During the year the Laboratory devised methods for judging the freshness of eggs (*cf.* ANALYST, 1938, **63**, 896), and the whiteness of flour, determining the "melting-line" of fats, and detecting casein in sausages.

Commercial tomato juice was found to contain the natural amount of vitamin C (13–20 mg. per 100 ml.), whilst a fivefold concentrated Hungarian product contained as much as 100 mg. per 100 ml.

J. STRAUB

CITY OF MADRAS

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1937

THE number of samples analysed under the provisions of the Madras Prevention of Adulteration Act, 1918, was 1094, as compared with 1039 in 1936. The samples comprised ghee and ghee mixtures (484), butter (122), milk (80), gingelly oil (263), ground-nut oil (71), coconut oil (30), coffee (20), tea (13), ghee substitutes (10), and other articles (1). Twenty-four of the gingelly oil samples were adulterated with ground-nut oil (10 to 90 per cent.), and 17 of the ground-nut oils were adulterated with gingelly oil (10 to 100 per cent.). One sample contained 40 per cent. of gingelly oil and 20 per cent. of coconut oil.

ADULTERATION OF GHEE.—Of the 484 samples examined, 153 were adulterated, almost entirely with hydrogenated oils in proportions ranging from 15 to 95 per cent. Butter is largely imported into Madras for making ghee either by the merchants or the consumers. As no preservatives are usually added to such butter, it soon begins to decompose and to have a bad odour, and this odour is retained by the ghee made from this butter. Most dealers convert all their unsold stock of butter into ghee, so that much ghee with a bad odour is also sold in Madras. Such butter or ghee is highly rancid and its sale should be prohibited in the interest of public health. It is suggested that the Government should fix a limit for the acid value of ghee and butter and that all products that exceed that limit should be destroyed, without, however, the vendors being subjected to prosecution.

V. VENKATACHALAM

Ministry of Health

FOOD AND DRUGS ACT, 1938

Circular 1755*

THE Minister of Health has issued a circular (dated December 15th, 1938) to all Local Authorities and Public Analysts on the new Food and Drugs Act passed last July. The Circular gives some account of the amendments in the law; it does not attempt to be exhaustive but elaborates certain points. For fuller explanations reference is directed to the report on a draft bill prepared by a Departmental Committee.†

Department of Scientific and Industrial Research

SIR FRANK SMITH, G.B.E., K.C.B., D.Sc., F.R.S., relinquished, on January 31st, his appointment as Secretary to the Committee of the Privy Council for Scientific and Industrial Research.

The King has approved the appointment of Professor E. V. Appleton, D.Sc., LL.D., F.R.S., to succeed Sir Frank Smith.

INDEX TO THE LITERATURE OF FOOD INVESTIGATION‡

As previously stated, steps are being taken to bring the *Index to the Literature of Food Investigation* up to date, and it is hoped to complete Vol. VII, No. 2, and Vol. VIII, which will deal respectively with the literature published in 1935 and 1936, within the next few months. Current literature is being dealt with at the same time, and the present issue (Vol. X, No. 2) deals with papers received between April 1st and June 30th, 1938. Henceforth each annual volume will be issued in four quarterly numbers, dealing respectively with papers received up to March 31st, June 30th, September 30th, and December 31st.

FOREST PRODUCTS RESEARCH

THE PRINCIPAL DECAYS OF SOFT WOODS§

This publication gives descriptions of twenty-six of the principal fungi that cause decay in soft woods used commercially in Great Britain, together with notes on their economic importance, and a key by which they may be identified. Speaking generally, timbers from coniferous trees, with a few important exceptions, are only moderately resistant to the attack of fungi and insects. Only two or three of the commercial softwoods used in this country can be considered as sufficiently durable to be used in an untreated condition in exposed situations. Species that are very resistant to decay include yew, cedars, Californian redwood and Southern cypress. Practically none of the very light-coloured soft woods (*e.g.* spruces and firs) are durable; those species that have a definitely coloured heartwood usually offer greater resistance to decay.

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1938. Price 2d. net.

† Third Interim Report of the Local Government and Public Health Consolidation Committee, Cmd. 5628. H.M. Stationery Office. Price 1s.

‡ H.M. Stationery Office, Vol. X, pp. 187. 1938. Price 4s. 6d. net.

§ H.M. Stationery Office, Forest Products Research Records, No. 7, 1939. Price 2s. 6d. net.

In timber that is properly stacked decay should never develop, but even when the timber is properly piled with adequate ventilation around the boards sap stain will frequently appear. To prevent the formation of such stain or of mould it is often necessary to dip the freshly-sawn boards in an antiseptic solution. It has been shown that the life of wood props can be extended from five to tenfold by an inexpensive treatment in an open tank with a solution of sodium fluoride or zinc chloride.

RISKS IN SURFACE CREOSOTING.—The growth of most fungi is inhibited by creosote, but one species, *Lentinus lepideus*, which is the most important fungus causing decay in railway sleepers, telegraph poles and wood-paving blocks, can withstand considerable amounts of that preservative. If the spores of the fungus can gain access through cracks to untreated wood in the interior of the timber, decay will spread throughout the whole piece. Sleepers may therefore appear superficially sound, while the interior is extensively decayed. Hence, to secure sufficient penetration of preservatives, it may be necessary to make incisions in certain timbers.

Federated Malay States

ANNUAL REPORT OF THE INSTITUTE OF MEDICAL RESEARCH FOR THE YEAR 1937

THE Director of the Institute (Dr. A. Neave Kingsbury) pays a tribute to the services of the late Mr. R. W. Blair, who had been connected with the Institute since 1912. His successor as Chief Chemist is Mr. Shelton, F.I.C.

The Chemical Division is mainly concerned with work connected with public health and police investigations. Of the 7436 samples analysed, 5091 were for the Medical and Health Services, 1317 for the Police, 1001 from other Government Departments and 27 from private persons. The Health Officers submitted 875 samples of milk of which 15·3 per cent. were watered and 1·7 per cent. contained less than the statutory 3·25 per cent. of fat. Twenty-eight samples complied with the legal standards, but were shown by their freezing-points to contain considerable amounts of added water.

REMOVAL OF BACTERIA WITH ALUMINIUM HYDROXIDE.—The results of many analyses have demonstrated that the precipitation of aluminium hydroxide in water can be a most efficient means of removing bacteria, especially if followed by mechanical filtration. Water thus treated does not readily develop algal growth in open reservoirs. Special treatment of the water is necessary to ensure the optimal *p*H for the aluminium hydroxide precipitation.

LEAD IN CANNED FOOD, ETC.—Fifty samples of canned products were examined. Of these, 27 were contained in crudely made tins in which the contents were exposed to a considerable surface of solder. Some of the tins showed evidence of having been previously used; with such there is a possibility of toxins from the original contents being present if cleaning before refilling has been inadequate. Seven samples of canned food contained lead equivalent to 5 or more parts of Pb per million.

The interiors of copper or brass cooking pots are usually tinned, but sometimes solder is substituted. There is a danger in the habitual storage of water overnight, either in these vessels or in soldered cans or in stoneware jars that may have lead glaze, for water in Malaya tends to be plumbosolvent.

In 29 cases of suspected lead poisoning the average lead-content of the urine was 0·3 p.p.m., but 1 p.p.m. was found in each of two samples from a Chinese.

In seven samples of canned peas copper (equivalent to 80 or more p.p.m. of Cu) had been added to improve the colour.

Motor Accident: Alcohol in Viscera.—In a case in which a pedestrian had been killed by a motor car, a sufficient quantity of alcohol was recovered from the viscera to indicate that the victim was intoxicated.

Camphor in Stomach Wash.—Camphor in small doses is sometimes used by labourers to reinforce the intoxicating power of stout and thus to achieve inebriation at a reduced cost.

Deciphering an Obliterated Document.—Some figures on a promissory note, written apparently with iron-gall ink, had been obliterated with ink of a similar character, but it was possible by means of infra-red photographs to reveal the original writing.

Government of Madras

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1937

The Report for 1937 has been drawn up by Mr. Rajagopal Naidu, F.I.C., who has succeeded Lt.-Col. Clive Newcomb as Chemical Examiner. It contains the usual account of poisoning cases, with details of those of special interest. The total number of cases of human poisoning was 426, as compared with 363 in 1936. Poison was detected in 255 cases. As in previous years, opium heads the list (38 cases), and is closely followed by oleander (33 cases). There was an increase in datura or mydriatic alkaloid poisoning (28 cases as against 11 in 1936), and there was also an increase in aconite poisoning (20 cases as against 5 in 1936). There were 13 cases of madar juice poisoning and 2 of oduvan poisoning. In 77 cases inorganic poison was detected—arsenic in 18, cyanide in 10, mercury in 15, copper in 8, nitric acid in 5, nitrite in 1. Among other points of interest reference is made to the following:

Nitrite Poisoning.—A woman swallowed a nitrite preparation used in the dyeing of cloths, and died in about 3 hours. At the post-mortem examination about ½ oz. of serous fluid was found in the pericardium, the right side of the heart was full of fluid blood, while the left side was empty. There was congestion of the lungs, spleen and kidneys, and the stomach contained a greenish fluid. Nitrite equivalent to about 33 grains of sodium nitrite was detected in the viscera.

Madar Juice Poisoning.—All the 13 cases were suicidal. Signs of cardiac failure were observed in 7 cases, intense congestion of the lungs in 9, congestion of the liver in 7, congestion of the stomach in 9, and of the brain in 4. In two cases madar juice was detected in the viscera (*cf.* Analyst, 1937, **62**, 741).

Croton Seed.—A woman who had been ailing from rheumatism was given a purgative by a quack. This caused incessant purging, which continued until the afternoon of the next day. Some "antidote" was then given, which stopped the purging, but the woman died in the evening. Particles of croton seed were detected in the paste that had been given as a purgative.

Identification of Croton, Castor, Jatropha and Jequirity.—A comparative microscopic study of the prismatic cells in the outer coats of these seeds has been found to be of use in their identification. The coats are cleared by immersion in 5 per cent. solution of potassium chlorate in dilute nitric acid over a boiling water-bath till the colour is bleached and the tissues are softened.

(i) *Cross-sectional view at the top.*—The cells in all four seeds are polygonal in shape, about 17μ in diameter in castor, croton and jatropha, and about 9μ in diameter in jequirity. The lumen is more or less circular in castor seed, slit-like in jatropha, and slit-like with radiating creases in croton and jequirity.

(ii) *Side view*—(*a*) *Length.*—The length of the cells is about 160μ in jequirity, about 250μ in castor, about 300μ in croton, and about 400μ in jatropha.

(*b*) *Width.*—In castor and croton the cells taper in width towards the bottom, the top width being about 17μ and the bottom about 8μ. In jatropha the tapering is less abrupt, the width at the top being about 17μ and that at the bottom being about 12μ. There is no appreciable tapering in the width of the cells in jequirity, which are about 9μ wide.

(c) *Lumen.*—All the cells in castor seed show a uniform lumen 3μ in diameter, and all the cells in croton show a uniform lumen about 1μ in diameter, whereas the cells in jatropha and jequirity show a uniform lumen varying in width in different cells from about 1 to 6μ in jatropha and from about 1 to 3μ in jequirity.

(d) *Walls.*—The cell-walls in castor and jatropha show fine transverse striae giving the cells a ribbed appearance. These striae are not noticeable in the cell-walls in croton and jequirity, and the cells do not show a ribbed appearance.

YELLOW OLEANDER SHELL.—The main frame-work of yellow oleander shells consists of characteristic fibres which are of use in identification. The clearing is done by a method similar to that described above. The cells from yellow oleander shells are sclerenchymatous fibres, spindle-shaped in appearance and varying in length from about 150 to 300μ, and in width from about 10 to 15μ. The fibres have pointed ends on both sides and a uniform lumen, about 2μ in diameter. The fibres may be stained with phloroglucinol and hydrochloric acid or with carbol-fuchsine.

DETECTION OF DATURA IN URINE.—In cases of datura poisoning examination of the urine appears to be more valuable than examination of the stomach wash. During the three years 1935, 1936, 1937, fourteen specimens of urine from victims of suspected datura poisoning were received, and in each a mydriatic alkaloid was detected. With only nine of the stomach washes was a positive result obtained.

ODUVAN LEAF.—The poisonous principle can be isolated in purer condition by extraction with alkaline ether than with the usual acid ether, tannins and other impurities being retained by the alkaline aqueous solution. The ethereal extract thus obtained is highly poisonous to frogs, and when treated with sulphuric acid gives a blue colour gradually changing to a permanganate tint. It does not give a green colour with conc. hydrochloric acid.

POISONOUS PRINCIPLE OF *Nerium odorum*.—This plant, known as *Kaner* (Hindustani), is very common in South India, and its leaves are often used as a poison, as either a paste or a decoction. Recent work on its poisonous principle does not support the conclusions of Chuni Lall Bose (*cf.* Lyon's *Medical Jurisprudence for India*, 8th Ed., p. 725). It is apparent that the three extracts referred to therein probably owed their poisonous action to one active poisonous principle, and that the three substances were probably the same poisonous principle in different degrees of purity. The pure white crystalline glucoside has been isolated from this plant and its chemical and physiological properties have been studied. The method of extraction was as follows:—The acid alcoholic extract of the leaves, after evaporation of the alcohol, was taken up with boiling water, the solution was treated with basic lead acetate and filtered, and the filtrate was decolorised with animal charcoal and again filtered. The cooled aqueous filtrate was de-leaded with sodium oxalate and filtered, and the filtrate made alkaline with sodium carbonate solution and extracted with chloroform. The chloroform extract, after removal of the chloroform by distillation, was dissolved in hot 30 per cent. alcohol, boiled with animal charcoal and filtered, and the filtrate was again extracted with chloroform. Evaporation of the chloroform at a low temperature and drying in the vacuum desiccator yielded a white crystalline substance (m.p. 123° C.), which was sparingly soluble in water, very sparingly soluble in ether, petroleum spirit or benzene, and readily soluble in alcohol, acetone or chloroform. A minute speck, dissolved in conc. sulphuric acid, gave an immediate purple colour which took on a deeper tint on standing. It also gave a positive result in Keller's test—a bright green colour appearing in the acetic acid layer and a purple colour in the sulphuric acid layer. Both the colours were stable for several days.

The average minimum lethal dose for frogs weighing about 10 g. was about 0·02 mg., paralysis and death being the symptoms noted. Eight mg., injected into the abdomen of a dog weighing about 4·1 kg., killed it within an hour. The symptoms noted were progressive paralysis starting from the hind legs, defecation, retching, foaming at the mouth and death. This extract was thus about six times as poisonous as strychnine to frogs.

Semi-micro combustion gave: C, 66·4; H, 8·08 per cent. (O, by diff. = 25·5 per cent.). The molecular weight was approx. 656. The formula $C_{35}H_{50}O_{10}$ and the name "nerin" are tentatively suggested for this substance. Quantitative determinations by Lane and Eynon's method, after hydrolysis with emulsin or hydrochloric acid, showed that 1 g.-mol. of the glucoside yielded 1 g.-mol. of a hexose calculated as dextrose. It was thus a β-glucoside. The non-sugar residue from the hydrolysis was much less toxic than the glucoside to frogs. The yield of pure "nerin" from the fresh leaves was about 0·09 per cent.

TESTS FOR QUININE.—Alkaloidal extracts from viscera are frequently received which are poisonous to frogs but do not give the reactions for known poisons. It is important to eliminate the possibility of the toxic principle in these extracts being quinine. About 1/40 grain of quinine is fatal to frogs, and none of the ordinary tests for quinine will identify such a small quantity. The fluorescence test (which is best applied by taking up a speck of the substance in a drop of dilute sulphuric acid, drawing this drop up into a silica capillary tube, and exposing it to ultra-violet light) is not specific for quinine and has at best only a negative value. The herepathite test was also found to be unsatisfactory with such small quantities of quinine.

Micro-chemical Reagent for Quinine.—A potassium iodide solution of iodine made strongly acid (about 5 *N*) gives a characteristic crystalline precipitate with quinine (*cf.* Gomberg, *J. Amer. Chem. Soc.*, 1896, **18**, 331; Abst., ANALYST, 1896, **21**, 193). The reagent is prepared by mixing 5 ml. of *N*/10 iodine in potassium iodide solution with 11 ml. of conc. hydrochloric acid (analytical reagent quality), and making up to 25 ml. with water or, preferably, glycerin. A drop of a solution of the suspected alkaloid in 5 *N* hydrochloric acid, when mixed on a microscope slide with a drop of the acid iodine solution gives, in the presence of quinine, sheaves of fine needles starting at the line of junction of the two drops and gradually spreading into the surrounding solution. Strychnine, brucine and quinidine give different forms of crystals. Aconitine, atropine, cocaine, cinchonine, cinchonidine and morphine in dilute hydrochloric acid solution yield no crystals with the reagent. The test can be used with solutions containing from 0·01 to 5 per cent. of quinine, and crystals are obtained with 1/200 mg. The test gave abundant crystals with the alkaloidal extract from viscera to which a fraction of a milligram of quinine had been added.

The reaction can be used for the quantitative determination of quinine or strychnine if interfering substances are absent (*cf.* Kippenberger, *Z. anal. Chem.*, 1895, **34**, 294; 1896, **35**, 10; Abst., ANALYST, 1895, **20**, 201; 1896, **21**, 191).

ESTIMATION OF PHENOL.—A rapid colorimetric method of estimating minute quantities of phenol, *e.g.* in urine, has been based on the colour produced on coupling diazotised *p*-nitraniline with the phenolic substance in the presence of sodium carbonate. The reagent consists of a solution of about 0·1 g. of *p*-nitraniline in 1 ml. of conc. hydrochloric acid, diazotised with saturated potassium nitrite solution at 80° C. until colourless, and diluted with 5 ml. of water. About 2 to 5 ml. of the distillate containing phenol are saturated with sodium carbonate in a Nessler cylinder and treated with 5 to 7 drops of the reagent. The solution is made up to the mark, and the colour is compared with known standards similarly prepared.

The method gives good results with solutions containing from 0·2 to 5 p.p.m. of phenol. The three cresols give colours of different intensity, and the method is therefore not satisfactory for mixed cresols, but if an actual sample of a mixture that has been swallowed is available, an estimation in terms of the mixture can be made.

IDENTIFICATION OF WIRES.—Suspected stolen wires which are of the same diameter as the original wires may be compared under the comparison microscope, and frequently it can be decided whether the two wires are from the same source of manufacture. In the process of manufacture the wires acquire minute lands and grooves due to slight imperfections in the dies through which they have been drawn to the thickness required. These lands and grooves are similar to the rifling marks produced on a bullet. In old rusty wires and wires that have received a coating of tin, the markings of the original die may be obscure. We found that immersion in hydrochloric acid for a few minutes dissolves out the copper oxide or tin without appreciably affecting the copper and leaves the original markings sufficiently distinct for comparison purposes.

IDENTIFICATION OF SEALING WAX.—A small particle of the wax is taken up with a few drops of alcohol, crushed, mixed and centrifuged. The clear alcoholic solution is taken up in a silica capillary tube (such as is used in the Marsh apparatus) and the fluorescence of the alcoholic solution in ultra-violet light is noted and compared with the fluorescences of other specimens similarly prepared. Comparisons of the fluorescences of different specimens of sealing wax may thus be made with very minute quantities of material, and the results are more decisive than when the sealing waxes themselves are exposed to ultra-violet light. The residue from the alcoholic solution, after being washed with alcohol and centrifuged, may be examined under the microscope as well as micro-chemically, and thus the nature of the filler in the sealing wax may be determined.

A sealed insured parcel of currency notes to the value of Rs.25,000 was sent from this province to a foreign place. The addressee found the seals intact but found inside the parcel only Rs.100 in currency notes, while newspaper and glass pieces formed the remainder of the contents of the parcel. The outer covering of the parcel was sent to us together with a specimen of the sealing-wax impression, the Customs declaration with a sealing wax impression on it, and a specimen of the thread with which the insured parcel was originally stitched. Under the comparison microscope the sealing wax impressions on the covering of the parcel and on the Customs declaration form were found to be identical with the specimen impressions. The material of the sealing wax was found to be identical in all three as shown by (1) the similar nature of fluorescence of the alcoholic solutions, (2) the same filler in each (calcium sulphate), and (3) nearly the same specific gravity. The conclusion was that the seal impressions, as well as the material of the sealing wax, were identical in all the three. Traces of destroyed seals were also found on the inner side of the hand-stitched portion.

The thread found in the stitches of the hand-stitched portion of the parcel corresponded with the specimen of thread sent by the police in (1) thickness, (2) the direction and angle of the twists, (3) the number of twists per unit length, (4) the number of strands twisted together, and (5) the material of the fibre (cotton). We found also remnants of severed stitches on the inside of the hand-stitched portion. It was therefore obvious that the originally sealed parcel had been opened, stitched and sealed again at the source.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Changes occurring in Eggs during Storage. I. The Occurrence of Methyl Ketones. F. Kiermeier and R. Heiss. (*Z. Unters. Lebensm.*, **1938, 76,** 530–534.)—Investigations concerning the changes occurring in eggs are usually undertaken to discover a method of determining the age of the egg, for statutory purposes, and involve the determination of "constants" which may vary widely. Since, for ordinary purposes, palatability is of more importance than the age of an egg, a more suitable criterion is one which has an initial zero value increasing with decomposition, such as the "decomposition-quotient" of Grossfeld and Peter (*Z. Unters. Lebensm.*, 1935, **69**, 16; Abst., ANALYST, 1935, **60**, 253), which is a measure of the decomposition of yolk-lecithin. During storage the taste of the yolk is affected first and, although many workers have sought to connect this with protein decomposition, it seems more likely, considering the high fat-content of egg-yolk, the large proportion of unsaturated acids in its component fatty acids, and the distinct effect upon taste of slight fat decomposition, that decomposition of the fat plays an important part. To detect fat decomposition the reaction for the detection of methyl ketones of Täufel and Thaler (*Chem.-Ztg.*, 1932, **25**, 265; Abst., ANALYST, 1932, **57**, 466) by the procedure of Schmalfuss, Werner and Gehrke (*Margarine Industr.*, 1932, **25**, 217), the peroxide reaction of Lea (*Proc. Roy. Soc.*, 1931, **108**, 175) and the reaction of von Fellenberg for the detection of aldehydes (Abst., ANALYST, 1925, **50**, 245; Pritzker and Jungkunz, *Z. Unters. Lebensm.*, 1926, **52**, 195; Abst., ANALYST, 1926, **51**, 635) were applied to the fat extracted from egg-yolk dried over anhydrous sodium sulphate. Tests applied immediately gave negative results. The peroxide reaction of Lea (*loc. cit.*) gave the following figures (ml. of $N/500$ sodium thiosulphate solution per g.) for the stated conditions of storage:—4 weeks at 20° C., 1·44; 3 weeks at 20° C. in the dark, 2·66; 3 weeks at 5° C., in a darkened refrigerator, 2·89. The aldehyde reaction of von Fellenberg did not occur with any of the above-mentioned samples. The methyl ketone reaction of Täufel and Thaler was given by the eggs stored in ordinary light at 20° C., and these eggs had the peculiar odour of undecyl-methyl ketone. Since the taste pointed to the occurrence of ketone rancidity, further experiments were limited to the detection of methyl ketones by Täufel and Thaler's salicylaldehyde reaction (*loc. cit.*). Eggs stored for 4 months at 0° C. and for 1 month at 20° C., answered to the test, but eggs stored for 2 months at 0° C. gave no reaction. Eggs stored for 4 months in an atmosphere containing 88 per cent. of carbon dioxide or for the same time in pure carbon dioxide answered only feebly to the test. In some instances the fat from eggs stored for 4 months responded to the test, but after 11 months storage gave no reaction. Similar behaviour has been found with lard, beef-fat and butter and by Schweigart and Heucke (*Vorratspflege u. Lebensmittelforsch.*, 1938, **1**, 195) with whole milk powder. It is probable that, although the ketones are formed initially, they are changed either by oxidation or by combination with subsequent products of decomposition.

Attempts to apply the quantitative, colorimetric method of Täufel, Thaler and Hohner (*Z. Unters. Lebensm.*, 1937, **74**, 119) for the determination of methyl ketones were not successful. It is possible that moulds accelerate the decomposition of the fat, since Starkle has shown (*Biochem. Z.*, 1924, **151**, 370) that fat, in the presence of moulds, may form methyl ketones but, since moulds are aerobic organisms, their presence does not explain decomposition during storage in inert atmospheres. Another explanation is suggested by the work of Knoop, who showed that in the organism fatty acids with an even number of carbon atoms may yield methyl ketones by β-oxidation. Although it has been established that methyl ketones are formed in yolk-fat, the experimental results are not yet sufficient to indicate a definite relation between the methyl ketone content and the palatability of the egg, but the work is being continued for this purpose. A. O. J.

Action of Milk upon Aluminium and its Alloys. G. Reif and H. J. Steinbeck. (*Z. Unters. Lebensm.*, 1938, **76**, 538–543.)—In previous work upon the action of fruit products upon aluminium and its alloys (*Z. Unters. Lebensm.*, 1937, **73**, 431) it was found that the corrosive properties of these acidic products are largely dependent upon their water-content and their aqueous extract. The greater the water-content the greater the corrosive action. It appeared also that the degree of dissociation of the extract plays an important part. With an amphoteric substance, such as milk, different results were obtained as might be expected. It is necessary to consider the effect of milk upon the external physical properties of the metal, since milk containers are subjected to much rough treatment. In general, aluminium alloys are harder than the pure metal, and the behaviour of these alloys is of special importance in the milk industry. With few exceptions it is evident that aluminium alloys show considerably more resistance to the action of milk than to the action of fruit products. The two specimens of aluminium available for this investigation contained 99·5 per cent. and 99·8 per cent. of aluminium respectively. The alloys used had the following percentage composition:—Pantal: silicon, 1·13; iron, 0·475; magnesium 0·74; manganese, 0·63; titanium, 0·03. Mangal: silicon, 0·39; iron, 0·25; manganese, 1·51. B.S.S. alloy: silicon, 0·12; iron, 0·18; magnesium, 6·82; manganese, 0·36. All specimens were used in the form of foil which was hard-rolled but not surface-treated, or which had been subjected to one of three processes for surface protection, *viz.* the modified Bauer–Vogel process (MBV) for surface protection by oxidation with sodium bicarbonate and sodium chromate, electrolytic oxidation in a sulphuric acid bath, and electrolytic oxidation in an oxalic acid bath. The pieces of foil were 1 mm. thick and measured 10 cm. by 4·9 cm. and weighed about 13 g. They were partly immersed in pasteurised milk which was raised to 100° C. in 45 minutes in an autoclave and heated under pressure for 35 minutes at 119° to 120° C. After this treatment the milk containing the foil could be kept for about six months at room temperature without decomposition. At the end of this period the changes in the properties of the metal were noted and the aluminium-content of the milk was determined by precipitation with 8-hydroxyquinoline and titration of the washed precipitate with potassium bromide-bromate solution according to Lehmann's modification (*Z. anal. Chem.*, 1927, **71**, 369) of the method of Berg

(*Arch. Hyg.*, 1931, **106**, 311). A comparison of the analytical figures found for the aluminium-content of the milk shows that the kind of surface treatment received by the metal has a greater effect than its composition upon its solubility in milk. The untreated foil in every instance showed a susceptibility to corrosion which was least in the pure aluminium foil and in the B.S.S. foil, greater in Mangal, and considerably greater in Pantal. The MBV process conferred good resisting properties throughout, although a somewhat greater solubility was shown by the B.S.S. foil that had been subjected to this treatment. The worst results were obtained with foil electrolytically oxidised in sulphuric acid, the most resistant of these being Mangal. Metal electrolytically oxidised in oxalic acid, on the other hand, possessed good resistance, but Mangal subjected to this process was slightly less resistant. It may be said that, as a rule, electrolytic oxidation in oxalic acid confers the greatest resistance, and that the MBV process is almost as effective. The least resistance was shown by metals subjected to electrolytic oxidation in sulphuric acid, and the untreated metals were somewhat more resistant. Of the two specimens of aluminium metal, the purer proved the more resistant, and both the untreated and the MBV-treated pure aluminium foils behaved equally well. Pure foil electrolytically oxidised in sulphuric acid had considerably lower resistant properties. Of the alloys, Pantal and B.S.S. alloy, electrolytically oxidised in oxalic acid, and Mangal treated by the MBV process gave the best results. It can be stated broadly that the alloys behaved as well as the pure metal and in some respects better; with fruit products the opposite result was obtained. There was complete harmony between the changes noted in the external properties of the samples and those determined chemically. The resistance of the alloys to the chemical and mechanical cleaning agents employed in the milk industry has not yet been studied. A. O. J.

Composition of Chinese Tea Seed Oil and of *Sterculia platanifolia* L. Oil. S. Ueno and T. Ueda. (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 326–328B.)—The Chinese tea seed oil (*a*) was of a pale brown colour and the *Sterculia* seed oil, (*b*) a pale orange-yellow, and the oils had respectively the following characteristics:—sp.gr. at 15/4° C., (*a*) 0·9166, (*b*) 0·9278; n_D^{20} (*a*) 1·4694, (*b*) 1·4722; saponification value, (*a*) 186·0, (*b*) 190·5; iodine value (Wijs), (*a*) 89·3, (*b*) 98·6; acetyl value, (*b*) 14·4; unsaponifiable matter, (*a*) 0·84, (*b*) 1·02 per cent.; acid value, (*a*) 4·4, (*b*) 2·5. The mixed fatty acids, freed from unsaponifiable matter, had n_D^{20}, (*a*) 1·4604; neutralisation value, (*a*) 195·6, (*b*) 198·9; iodine value, (*a*) 99·0, (*b*) 99·2. Separation by the lead salt and alcohol method yielded solid acids, (*a*) 6·3, (*b*) 24·8 per cent.; of m.p., (*a*) 59·0° C., (*b*) 58·8° C.; neutralisation value, (*a*) 198·7, (*b*) 208·1; liquid acids, (*a*) 93·7, (*b*) 75·2 per cent.; of n_D^{20}, (*a*) 1·4604, (*b*) 1·4720; iodine value, (*a*) 99·6, (*b*) 125·3; neutralisation value, (*a*) 193·2, (*b*) 187·8.

Methylation and fractionation of the solid acids under a reduced pressure of 2 mm. and fractionation of the methyl esters of the liquid acids, together with Hazura's oxidation test and the bromide test showed that the 6 per cent. of solid acids in Chinese tea seed oil consisted of palmitic and stearic acids and the liquid acids of 90 per cent. of oleic and 10 per cent. of linolic acid. The solid acids of *Sterculia platanifolia* were treated similarly and the methyl esters of the liquid

acids were distilled to give 5 fractions. Fractions 4 and 5 were mixed and redistilled, and the fatty acids from fraction 2 were separated by the lithium salt and alcohol method, whereby oleic acid was identified. The bromide test yielded a bromide of α-linolic acid. The 25 per cent. of solid acids of *Sterculia* oil are regarded as composed chiefly of palmitic with some stearic acid, and the liquid acids of about 60 per cent. of oleic and 40 per cent. of linolic acid with some C_{20} acid (?).
D. G. H.

Composition of Papaw Seeds (*Asimina triloba*). J. L. Riebsomer, J. Bishop and C. Rector. (*J. Amer. Chem. Soc.*, 1938, **60**, 2853–2854.)—The ripe fruits of *Asimina triloba* (the papaw), used in this investigation were obtained from Putnam county, Indiana, and the seeds were freed from pulp and dried at room temperature. Each fruit contained from 2 to 12 flat, oblong, dark brown seeds of an average weight of 0·7 g. The air-dried seeds were ground, and dried at 100–110° C. in an atmosphere of carbon dioxide, with a loss of 5·1 per cent. The dried residue, extracted with petroleum spirit, yielded 38 per cent. of a reddish-brown fatty oil, leaving a slightly grey residue. The oil had the following characteristics:—sp.gr. at 25/25° C., 0·9296; n_D^{25}, 1·4728; saponification value, 194·0; iodine value (Hanus), 113·5; Reichert-Meissl value, 1·05; acetyl value, 18·11; acid value, 6·4; unsaponifiable matter, 0·8 per cent.; saturated acids, corrected, 5·6 per cent., of mean molecular wt. 307·9 and iodine value 14·0; unsaturated acids (checked by lead-salt method), 85·5 per cent., of mean molecular wt. 308·2 and iodine value 117·8. The composition of the unsaturated acids was determined by distillation of the methyl esters at 4 mm. pressure, reduction of unsaturated methyl esters with hydrogen, by the bromine test, and by the ozonolysis method of Riebsomer and Johnson (*J. Amer. Chem. Soc.*, 1933, **55**, 3352) applied to the unsaturated methyl esters; the results indicated 69·5 per cent. of oleic and 30·5 per cent. of linolic acid. The methyl esters of the saturated acids were also distilled and the fractions examined. The saturated acids appeared to consist approximately of palmitic acid, 41·5; stearic acid, 31·8; arachidic acid, 26·6 per cent. The ground dried seeds contained protein 1·128, crude fibre 20·0, and ash 1·3 per cent.
D. G. H.

Rice Oil. Constituents of the Liquid Acids. S. Ueno and T. Ueda. (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 325–326B; *cf. ibid.*, 1937, **40**, 200B.)—This investigation concerns the C_{18} acids of rice oil. The clear rice oil used had the following characteristics:—sp.gr. at 15/4° C., 0·9266; n_D^{20}, 1·4770; saponification value, 183·1; iodine value (Wijs), 106·9; acid value, 29·5. The mixed fatty acids had neutralisation value 191·5 and iodine value 112·0, and separation by the lead salt and alcohol method yielded 86·6 per cent. of liquid acids of neutralisation value 198·7, and iodine value 127·2. Fractionation of the methyl esters of the liquid acids at a pressure of 2 mm. yielded 6 fractions which were analysed. Oxidation of the liquid acids by Hazura's method of permanganate oxidation yielded a white crystalline solid (m.p. 135–135·5° C.), identified as dihydroxystearic acid. Linolenic acid was not found and bromination yielded α-linolic acid bromide. The liquid acids of clear rice oil were thus found to consist of about 50 per cent. of oleic and 50 per cent. of linolic acid.
D. G. H.

Bitter Constituents of Navel and Valencia Oranges. R. H. Higby. (*J. Amer. Chem. Soc.*, 1938, **60**, 3013–3018.)—The Valencia and Navel oranges of California are equally good for general use, but the juice of the Navel variety, when exposed to air or pasteurised, develops a bitter taste and astringency, depending in degree on the maturity of the fruit and usually disappearing with the warm weather in March and April. The bitter principle of the Navel orange was isolated by extraction with benzene and treatment with petroleum spirit followed by purification. Tests on the pure substance showed it to be isolimonin, previously reported as a constituent of orange seeds. A higher molecular weight is indicated than has been previously reported, and corresponds to a formula $C_{26}H_{30}O_8$, and the substance appears to be an isomer both of limonin and of citrolimonin. It was present in the albedo and the section covering of the fruit, as a non-bitter water-soluble form. Rupture of the tissues brings it into contact with the juice, and it then becomes changed into the intensely bitter lactone form. Acid hydrolysis of the isolimonin in acetone yielded fractions of limonin and of hexahydrolimoninic acid. This latter substance had previously only been obtained by catalytic hydrogenation of limonin. Apparently limonin results from a molecular rearrangement in the isolimonin and hexahydrolimoninic acid by the splitting of a lactone ring to form a carboxyl group. Limonin (not isolimonin) was isolated from Valencia oranges following a similar type of extraction treatment to that used with the Navel oranges. D. G. H.

Characteristic Property of Tobaccos of the Alkaline Group. A. Wenusch and R. Schöller. (*Z. Unters. Lebensm.*, 1938, **76**, 546–548.)—The physiological action of tobacco preparations made from tobaccos of the alkaline group (chiefly cigars) depends upon the high evolution of nicotine characteristic of the alkaline tobaccos. This bears no relation to the total nicotine-content. Experiments show that a distinct relation exists between the amount of nicotine in the smoke and the amount of basic substances obtained by distillation of the tobacco with water without any addition of alkali. The tobacco (10 g.) is finely powdered, mixed with 500 ml. of water and distilled in steam until the distillate is free from nicotine and no longer alkaline. The distillate, which may reach 4 to 5 litres, is treated with 10 to 60 ml. of $N/10$ hydrochloric acid according to the amount of basic substance expected and the mixture is back-titrated with $N/10$ sodium hydroxide solution, methyl red being used as indicator. After acidification with dilute hydrochloric acid, it is concentrated *in vacuo* to 100 to 200 ml., treated with 5 ml. of dilute hydrochloric acid (1 : 4) and 5 ml. of 12 per cent. silicotungstic acid solution and allowed to stand overnight. The precipitate is separated, washed with 0·1 per cent. hydrochloric acid, dried at 120° C. and weighed. The filtrate, containing the volatile bases not precipitated by silicotungstic acid, is rendered alkaline with potassium hydroxide solution and again distilled. The distillate is titrated with $N/10$ hydrochloric acid. By this procedure three values are obtained which serve to identify tobaccos of the alkaline group, *viz.* the total amount of basic substance volatile on distillation of the tobacco with water without the addition of alkali; the fraction of this precipitated by silicotungstic acid (nicotine); the fraction not precipitated by silicotungstic acid. The following results are extracted from the table given. A high quality Havana tobacco gave 2·55 per cent. of total nicotine, 1·63 per cent. being volatile in steam without addition of alkali. The proportion of the total volatile bases not precipitated by silicotungstic acid was 85·9 per cent. Maryland tobacco, also of the alkaline group, gave 1·34 per cent. of total nicotine and 0·19 per cent. of bases directly volatile in steam, and the proportion of basic substance precipitated by silicotungstic acid in the total volatile bases was 71·0 per cent. In contrast with these, Nigritta, a tobacco of the acid group, gave a slightly acid distillate (*p*H 4·7), a total nicotine-content of 0·69 per cent. and no bases directly volatile in steam. A. O. J.

Biochemical

Significance of the Zinc-Content of Commercial Samples of Insulin. E. H. Vogelenzang and L. A. Hulst. (*Pharm. Weekblad*, 1938, **75**, 1390–1392.)—Scott (*Biochem. J.*, 1934, **28**, 1592) has found that the presence of zinc or of an allied metal (*e.g.* cadmium) is necessary in order to obtain insulin in a crystalline state, and that the rate of therapeutic action of such crystalline preparations is slower than that of amorphous insulin having a very low metal-content. Sahyun (*Arch. Intern. Med.*, 1937, **59**, 335) ascribed this difference to a change in the molecular structure of the insulin, whilst Rabinowitch (*Canad. Med. Assoc. J.*, 1936, **35**, 239) inferred that the zinc ion has a specific inhibiting effect, since he found a similar slow rate of action when using a solution of ordinary insulin to which was added a zinc salt. Wij (*Ned. Tijdschr. v. Geneesk.*, 1936, **80**, 4128; 1937, **81**, 1916, 3525) obtained similar results when comparing protamine insulin and protamine zinc insulin. The present authors found the following zinc-contents (in mg. per 1000 units) for samples of insulin received in March, 1937, and monthly from January to July, 1938, inclusive:—0·060, 0·005, 0·055, 1·78, 1·75, and 2·04, 1·90, 1·25, 0·60, respectively. The clinical results were correlated with these variations in zinc-content. Since insulin which has been crystallised with the aid of added zinc contains 2 mg. of zinc per 1000 units, it is evident that untreated insulin may contain variable quantities of zinc, which may have appreciable clinical effects, especially in view of the period that may elapse between the administration of the insulin and the response of the individual, as indicated by the blood-sugar content. Possible cases in which such variations might have serious consequences (*e.g.* when a series of daily injections is being given) are discussed, and a plea is made for a commercial insulin of standardised zinc-content. (See also R. S. Aitken, *Lancet*, 1938, **235**, 768.) J. G.

Standardisation of 2 : 6-Dichlorophenolindophenol with Ferrous Compounds. A. J. Lorenz and L. J. Arnold. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 687.)—As a result of the observation that the presence of ferrous ions in canned fruits and fruit juices interfered with the titration of ascorbic acid by 2:6-dichlorophenolindophenol, the use of ferrous salts for standardising solutions of the dye was investigated. It was found that the reaction between ferrous salts and the dye was very slow in the presence of most acids, but was rapid and quantitative in the presence of metaphosphoric or oxalic acid. The following method is therefore proposed for standardising the dye solution. One g. of ferrous ammonium sulphate is dissolved in water, 10 ml. of conc. sulphuric acid are added, and the solution is made up to 1 litre. Five to 10 ml. of a saturated (4 per cent.) solution of oxalic acid or of 3 per cent. metaphosphoric acid are added to 2 to 5 ml. of the ferrous solution, which is then titrated with 2 : 6-dichlorophenolindophenol solution. One mol. of the dye is equivalent to two atoms of iron, so that

$$1 \text{ mg. of ascorbic acid} \equiv 0{\cdot}634 \text{ mg. of Fe.}$$

The method is claimed to be more accurate than that of Menaker and Guerrant (*cf.* ANALYST, 1938, **63**, 201), using potassium iodide as standard, as it gives almost the same value as that obtained by the iodine and ascorbic acid titration.

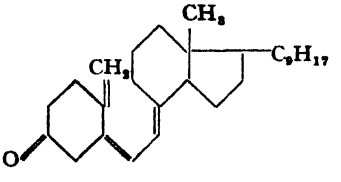
F. A. R.

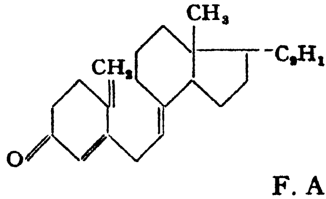
Vitamin C Content of Esthonian Honey. M. Kask. (*Z. Unters. Lebensm.*, 1938, **76**, 543–545.)—Experiments show that honey may contain an average amount of 4·88 mg. of ascorbic acid per 100 g.. With this amount success with animal feeding tests is not to be expected, and this may explain the statement frequently encountered that honey contains little or no vitamin. Honey (10 g.) was mixed with 10 ml. of 8 per cent. acetic acid and 10 ml. of distilled water and titrated directly with 0·2 per cent. 2 : 6-dichlorophenolindophenol solution, and another portion similarly prepared was titrated with $N/100$ iodine solution. Apparently, honey contains substances which increase the amount of reagent required for titration, the error being about 10 per cent. for the dye solution and considerably more for the iodine solution. Consequently, the iodine method was ultimately abandoned. The vitamin C content of 160 samples was determined. Of these, 9 were adulterated with artificial invert sugar and 7 with starch syrup. The genuine samples gave an average vitamin C content of 4·88 mg. per 100 g., the highest value for an individual sample being 20 mg. The 9 samples adulterated with artificial invert sugar gave an average figure of 1·6 mg. per 100 g., the lowest figure being 0·8 and the highest 4·2. The 7 samples adulterated with starch syrup gave an average content of 12·9 mg. per 100 g., the lowest figure being 4·8 and the highest 30·7. The majority of the unadulterated samples contained about 2·8 mg. per 100 g. Four samples containing no vitamin C were from bees fed with cane sugar, and were colourless with a high sucrose-content and a low diastatic value. Honeys containing little vitamin C were mostly pale coloured; those rich in the vitamin were brown or dark brown and, of these, four were authentic pine honeys. The samples adulterated with artificial invert sugar contained little vitamin C; those adulterated with starch syrup, relatively more. The vitamin-content of samples kept at 18° C. diminished by the following amounts:—one year, 10 per cent.; two years, 25 per cent.; three years, 50 per cent. This stability of the vitamin C in honey was also noted by Griebel (*Z. Unters. Lebensm.*, 1938, **75**, 417; Abst., ANALYST, 1938, **63**, 516). The vitamin-content is unaffected when honey is heated for one hour at temperatures between 60° and 100° C. Although, with the exception of the pine honeys and the *Mentha* honey examined by Griebel (*loc. cit.*), honey cannot be regarded as a rich source of vitamin C, its vitamin-content should not be overlooked.

A. O. J.

Constitution of the Antirachitic Vitamin from Tunny Fish Liver. H. Brockmann and A. Busse. (*Z. physiol. Chem.*, 1938, **256**, 252–270.)—The antirachitic vitamin previously isolated in the form of a resin from tunny fish liver oil by way of the crystalline 3 : 5-dinitrobenzoate has itself now been obtained in crystalline form, m.p. 82–84° C., by using larger amounts of material than before. The crystalline vitamin appeared to be identical in all its properties with synthetic vitamin D_3, and had a biological activity of 40,000 i.u. per mg. Its m.p., however, and those of its dinitrobenzoate and *p*-nitrobenzoate differed by a few degrees from the m.p. of the synthetic vitamin and its derivatives. It was suspected that the reason for this was the presence of vitamin D_2, and it was, in fact, shown that a mixture of vitamin D_3 with 10 per cent. of vitamin D_2 closely resembled the vitamin from tunny fish liver oil. It being impossible to separate the two vitamins from one another by fractional crystallisation, or by fractional crystallisation of their esters or other derivatives, the presence of vitamin D_2 had to be proved by an indirect method. From the products of ozonolysis of vitamin D_2, methylisopropylacetaldehyde can be isolated, but this is not formed on ozonolysis of vitamin D_3. The vitamin from tunny fish liver oil was therefore ozonised and the product steam-distilled; methylisopropylacetaldehyde was isolated from the steam distillate as its 2:4-dinitrophenylhydrazone. By this investigation the existence of vitamin D_2 (calciferol) in a natural product, namely, a fish liver oil, is established. F. A. R.

Ketone from Vitamin D_2 (Calciferol). A. Windaus and K. Buchholz. (*Z. physiol. Chem.*, 1938, **256**, 273–276.)—Calciferol was dehydrogenated by aluminium butylate to a ketone. This has not yet been obtained in crystalline form, but it gave a crystalline semicarbazone, m.p. 218–222° C. with an absorption maximum at 293*mμ*. The ketone regenerated from the semicarbazone had an absorption maximum, like that of calciferol itself, at 265*mμ*. It had 1/300 the vitamin D activity of calciferol. Its constitution is not yet established and it may have either of the following structures:





F. A. R.

Bacteriological

Vi Agglutination in the Diagnosis of Typhoid Fever and the Typhoid Carrier Condition. S. S. Bhatnagar. (*B. Med. J.*, 1938, 1195–8.)—In the examination of 235 typhoid strains collected from different parts of the world the author has identified one that behaves like a pure Vi variant which he designated Vi 1. This is not only insensitive to O and H antiserum but more sensitive to Vi than any strain yet found. With this strain, together with O and H strains, the author has carried out an extensive investigation of the agglutinations given by the blood of 134 cases of typhoid fever collected every fourth day. The results, which are set out in tabular form, show that Vi antibody was present in every case of typhoid fever whether previously inoculated or not. A distinct difference, however, was seen to have been caused by inoculation, so far as the titre of this antibody was concerned, in that the blood of the inoculated individuals generally gave a higher reading. In sixteen cases the blood was examined every third day, and the results, plotted in graphs, show a steeper rise in antibody with those individuals who were previously inoculated. From the point of view of diagnosis of acute typhoid condition with the aid of Vi agglutination the author has found that in an inoculated community a definite conclusion can be arrived at by the end of the first week when a titre of 1–25 to 1–50 is given. In an uninoculated population, however, a negative Vi agglutination cannot be relied upon to exclude typhoid infection until a much later date, though generally agglutination is shown by the end of the second week when a typhoid infection exists. Vi agglutination is of particular value in the detection of the typhoid carrier condition, for normally the blood of convalescents shows only traces of Vi antibody, whilst chronic carriers have been found to retain this antibody. When, therefore, Vi agglutination is given, thorough and repeated search for *B. typhosus* in the stools and urine is indicated. In testing for Vi agglutination the usual technique must be modified. Dreyers tubes are unsuitable and the author recommends round-bottomed tubes about 5 cm. long with uniform internal diameter of about 1·25 cm. The difference between the agglutinated bacteria and those that have simply settled can be easily made out in these tubes by shaking the whole serum-suspension mixture, the agglutinated bacteria then become readily visible as a considerable mass of somatic agglutination. Formalised suspensions of the strain Vi 1 can be used and give reliable results for a period of 4 to 10 weeks; it is advisable, however, to test frequently against Vi serum of known titre. D. R. W.

Differentiation of Wood-decaying Fungi by their Reactions on Gallic or Tannic Acid Medium. R. W. Davidson, W. A. Campbell and D. J. Blaisdell. (*J. Agric. Res.*, 1928, 57, 683–95.)—Following up the observation of Bavendamm that species of fungi causing white decay formed a dark diffusion zone or "corona" under the fungus mats when grown on media containing small amounts of gallic and tannic acids, whereas those causing brown checked decay gave no such reaction, the authors have investigated 210 fungi and classified them into 10 groups according to their growth or failure to grow on 0·5 per cent. gallic acid or tannic acid malt agar, with the production of dark diffusion zones (considered to be due to the presence of oxidase in the fungus) in the presence of one or other or both of these acids. A description of the medium employed is given: the malt agar is sterilised in the autoclave at 115° C., the gallic acid or tannic acid is dissolved in autoclaved distilled water at about 100° C., and the requisite amount is added to the malt agar when cool enough to handle just before pouring into Petri dishes. This medium has a milk-white appearance. Observation of the intensity of reaction and growth of mycelium was made after incubating at 25° C. for 7 days, and in doubtful experiments the cultures were kept for an additional 7 days. The reactions of these fungi are set out in tabular form, and the paper includes three plates showing eighteen photographs of colonies of fungi illustrating the different appearances that may be presented. Twenty-nine, or 80 per cent., of the fungi associated with brown carbonising rots gave no reaction with gallic or tannic acid media. One (*Fistulina hepatica*) associated with a dark firm rot, was negative, as was also *Stereum frustulosum*, associated with a white pocket rot, and *Polyporus dichrous*, associated with a white rot. Four, whose rots were unknown, gave no reaction. Seven fungi associated with brown carbonising rots gave inconsistent reactions. One hundred and fifty-six, or 96 per cent., of those fungi associated with white rots gave positive reactions. Nine specimens, whose rots were unknown, also gave positive reaction. *Stereum subpileatum*, associated with a white pocket rot similar to that of *S. frustulosum* gave mostly positive results on gallic acid, but was negative on tannic acid media. *Schizophyllum commune*, a white rot fungus, was negative on gallic acid medium, but positive on tannic acid medium, with good growth on both media. D. R. W.

Agricultural

Lactate Method for the Determination of Readily-soluble Phosphoric Acid in Soils. H. Egnér, G. Köhler and F. Nydahl. (*Annal. Landwirthschl. Hochschule Schevedens*, 1938, 6, 253–298.)—The samples are taken by means of a borer having a diameter of 1·5 to 2·0 cm., so as to eliminate stones; 3 to 4 should be taken per hectare, and the total sample should weigh about 500 g. It is dried in air, pulverised and passed through a 2-mm. sieve, and the residue is weighed (see below). Five g. of the air-dry powdered sample are then extracted for 2 hours (±10 minutes) at 20° ± 1° C., with 250 ml. of a solution prepared by adding 100 ml. of 5·0 *N* hydrochloric acid to a solution of 152 g. of calcium lactate in 0·7 to 1 litre of boiling water, this mixture being diluted to 2 litres when cool, and preserved by the addition of a drop of chloroform or xylene. This solution is stable in the dark (any deposit formed may be ignored), and it should be diluted 25-fold just before being used for the extraction; it has *p*H 3·7. Since the water-content of calcium lactate may vary, it is advisable to determine the equivalent weight by ashing the reagent, and back-titrating a solution of the ash in an excess of standard hydrochloric acid with sodium hydroxide solution. The extraction of the soil is conveniently made in mineral water bottles with spring-stoppers, and 60 to 90 of these may be used at once in the shaking apparatus described. The mixtures are all filtered together, the first 20 ml. of filtrate being rejected, and the colorimetric determination of the phosphate is made on the filtrate (*which must be clear*) on the same day as the extraction, as follows:—To 25 ml. of extract at 20° C. is added 1 ml. of a solution prepared by dissolving 50 g. of granular ammonium molybdate in 500 ml. of water at a temperature below 60° C., and adding 1 litre of 50 per cent. (by vol.) sulphuric acid; the mixture should be made with both solutions at 20° C., and, after shaking, 2 litres of water are added, and the resulting solution is stored in an amber bottle. A filtered solution containing 12 g. of stannous chloride ($SnCl_2,2H_2O$) in 1 litre of 3·0 *N* hydrochloric acid is also prepared, and the strength is adjusted to 0·0886 *N* by the addition of more 3·0 *N* hydrochloric acid, the volumetric iodine method being used to check the strength. This solution should be stored in completely-filled bottles, and 0·5 ml. of it is added to the mixture of the sample and the molybdenum reagent, in strong daylight. The resulting blue colour is matched within 15 to 20 minutes. The match may be made colorimetrically against standard solutions prepared from potassium dihydrogen phosphate, which are treated by exactly the same procedure, but a photo-electric selenium cell colorimeter is also described in great detail. The principal advantage of the latter is rapidity of operation, this being essential when a large number of samples have to be evaluated in the specified time. It comprises a vertical containing-vessel of rectangular cross-section for the solution; this vessel may be filled with solution or washing-water from above, and emptied rapidly from below without the necessity of removing it from the apparatus; there is also an adjustable diaphragm, which increases the range of the instrument by allowing the passage to the photo-electric cell of varying quantities of light. The apparatus must first be calibrated in terms of solutions of known phosphate-contents. The presence of much humus may result in a yellow colour, but this is not usually a serious source of error. The lactate value (L) is the number of mg. of soluble P_2O_5 in 100 g. of powdered air-dry sample. If the soil contains much lime, the pH of the extracting solution may be affected, and the rate of solution of the phosphoric acid is consequently decreased. In such cases 50 ml. of the extract are tested with bromophenol blue, and if the pH exceeds 4 and the lactate value is less than 10, the residual soil is re-extracted with 250 ml. of lactate solution; or, alternatively, the extraction may be repeated, using 1 g. of the original sample and 250 ml. of lactate solution and an extraction-period of 2 hours. The corrected lactate values are then, respectively, $(L_1 + 0{\cdot}5L_2)$ and $3{\cdot}3 \times$ lactate value found. The factor 3·3 is a mean figure established experimentally. The humidity value (F) is determined by bringing the powdered air-dry sample into equilibrium with air of 50 per cent. relative-humidity at 20° C., and then determining the loss in weight on further drying at 100° to 105° C. for 18 hours; F is expressed as a percentage of the weight at 50 per cent. R.H. Similarly, the ash value (G) is the loss in weight on ignition of the sample dried at 100° to 105° C. calculated as a percentage on the weight of the sample at 50 per cent. R.H. An apparatus for adjusting the humidity of a large number of samples to 50 per cent. is described, in which air is passed through a solution containing 43 g. of sulphuric acid per 100 g. and circulated at the rate of 5 litres per minute through a box at $20° \pm 1°$ C. containing trays on which are placed 5 g. of the samples in porcelain dishes (50×25 mm.). If T and H are the clay and humus contents of the soil, respectively, then for many soils $T = (10F - 2G)$, and $H = (1{\cdot}1G - 0{\cdot}5F)$. In exceptional instances special determinations of the constants used in the above equations are necessary. Nomograms for these expressions are provided, and they also enable corrections to be made for any stones and gravel present. The volume-weight (V) is the weight (in g.) of soil occupying a volume of 1 ml., and it is determined by placing a known weight of the sample in a 100-ml. graduated cylinder, which is shaken 200 times in a vertical direction, the amplitude of the shake being 5 cm. and its frequency 1 per second; a suitable apparatus is described. If the pH of the soil is also determined (*e.g.* with the quinhydrone electrode), then the phosphate value (*i.e.* the number of kg. of plant-available P_2O_5 per hectare of soil) is given by

$$P = LMV[1 - (S_1/100)^{3/2}][1 - \mathrm{S}_2/200]f_1(p\mathrm{H})f_2(FG)$$

where S_1 is the percentage of the surface of the soil represented by stones; S_2, the percentage of gravel, as determined by the sieve-test (see above) on the air-dry sample; M is the depth of the layer of soil in cm.; f_1, the correction factor for the pH of a suspension of soil in water, is 1, 0·6 or (10–pH)/4 according as the pH is below 6, over 7·5 or 6 to 7·5, respectively; and f_2, a constant depending on the nature of the soil, may usually be taken as $(1 + F - 0{\cdot}2G^2)/1{\cdot}25$. When P is less than 150 and the pH exceeds 6·5, this is an indication of phosphate-shortage; if, however, P exceeds 250, the soil is regarded as rich in phosphorus. Special allowance in sampling should be made with plants having long roots (*e.g.* sugar-beet), which penetrate to relatively great depths of soil. J. G.

Organic

New General Reaction for Enolic Forms: Mercurous Nitrate. Mechanism of the Reaction. E. V. Zappi and A. Manini. (*Anal. Asoc. Quím. Argentina,* 1938, **26**, 89–105.)—In previous papers (Zappi, *Anal. Asoc. Quím. Argentina*, 1931, **19**, 199; *Bull. Soc. Chim. de France*, 1932, **51**, 54; Abst., ANALYST, 1932, **57**, 330; Zappi and Williams, *Anal. Asoc. Quím. Argentina*, 1932, **20**, 147; *Bull. Soc. Chim. de France*, 1932, **51**, 1258; Zappi and Manini, *Anal. Asoc. Quím. Argentina*, 1934, **22**, 21) it has been shown that mercurous nitrate is a reagent (Zappi's reagent) for compounds containing the enol group ($-C(OH){=}CH-$), imino alcohols ($-C(OH){=}NH$), thio-imino alcohols ($-C(SH){=}NH$), isonitriles (${=}C{=}NH$), allyl compounds ($-CH_2-CH{=}CH_2$), or acetylenic compounds ($-C{\equiv}C-$). Metallic mercury is precipitated and there is formed a complex containing mercury and the organic compound. The authors present evidence to show that in mercurous compounds there exists a state of equilibrium represented by the equation

$$Hg_2(NO_3)_2 \rightleftharpoons Hg + Hg(NO_3)_2,$$

and that the addition of the active organic compound upsets this equilibrium, causing the precipitation of mercury and the formation of a complex of the organic compound and mercuric nitrate; the complex is, in general, only slightly soluble and somewhat unstable, but allyl alcohol and pyridine give complex compounds which are soluble in hot water and insoluble in cold water, so that they can be purified and their composition determined. According to the authors' theory, treatment of mercuric nitrate with an active organic compound should yield the same complex as with mercurous nitrate, but without the precipitation of metallic mercury; this was proved to occur with allyl alcohol and pyridine. The hypothesis advanced by Dansi and Sempronj (*Gazz. Chim. Ital.*, 1933, **63**, 560) that there are first formed complex compounds containing mercuric nitrate and that these immediately decompose to give metallic mercury and complexes containing mercurous nitrate is thought to be improbable, partly because no such mercuric nitrate complexes have been described in the literature. E. M. P.

Estimation of Amylases by Liquefaction of Starch-paste. J. Blow and A. Bak. (*Z. physiol. Chem.*, 1938, **256**, 197–207.)—The rate of hydrolysis of starch has been used previously to determine the activity of enzyme preparations, the hydrolysis being followed by measuring the viscosity of the solution at intervals.

The chief objection to the method is that the use of a different starch or slight variations in the method of making the starch-paste has led to variations in the viscosity of the latter and so to variations in the apparent enzyme-activity. For this reason the authors made use of a standard solution of sucrose, and calculated the time (in seconds) at which the viscosity of the amylase-starch paste mixture was (*a*) double that of the standard (t_1), and (*b*) equal to that of the standard (t_2). Then $t_2 - t_1$ is the time required for 1 g. of amylase to reduce the viscosity of a starch-paste from twice that of a standard solution to that of the standard. The "enzyme activity" is expressed as $\frac{1000}{a(t_2 - t_1)}$.

Preparation of the starch-paste.—Sufficient potato-starch to give 15·0 g. of pure starch is transferred to a 500-ml. flat-bottomed flask and water added to give a total weight of 375 g. The suspension is stirred for one minute with a high-speed mixer, and 40·0 ml. of 2 *N* sodium hydroxide solution are added. The mixture is again stirred, producing, after half-a-minute, a highly viscous mass. The stirring is continued for a further 15 minutes, during which time the viscosity slowly falls, and then 40 ml. of 3 *N* acetic acid are added, which causes a sudden fall in the viscosity. After being stirred for a further 30 minutes, the contents of the flask are diluted to 500·0 g. with water, and the mixture is stirred for another minute. The paste so prepared is quite uniform and has a viscosity at 20° C. some 40 times that of water. Its *p*H is about 5, this being the optimum *p*H for malt amylase. If pancreas amylase is to be tested, 20·0 ml. of *N* hydrochloric acid and 40·0 ml. of *N* phosphoric acid should be added instead of the 40 ml. of 3 *N* acetic acid. The *p*H of the resulting paste is then 6·8, and the chloride ion concentration is optimal for pancreas amylase.

Measurement of rate of hydrolysis.—An Ostwald viscometer is calibrated by means of a 45 per cent. sucrose solution at 20·0° C., a viscometer with an outflow time of 60 to 90 seconds being chosen. The bulb and capillary are jacketted, and the whole is clamped above a 100-ml. flat-bottomed flask, so that the tip of the viscometer just touches the bottom of the flask. A mixture of 5·00 ml. of the enzyme solution and 50·0 g. of the starch-paste are placed in the flask, which is then immersed in a thermostat maintained at 20·0° C. Water from this is circulated through the jacket enclosing the viscometer by means of a small pump. From time to time during the hydrolysis a little of the mixture is drawn into the viscometer, and the time taken for it to run out is measured. This is repeated as often as necessary until the time is less than that taken by the standard sucrose solution. The time (t_2) taken for the viscosity of the mixture to fall to a value just equal to that of the standard solution is calculated by interpolation. A second experiment is carried out, using exactly $\frac{1}{4}$ or $\frac{1}{5}$ the weight of enzyme preparation (in 5 ml.), and the time taken for the viscosity to reach a value double that of the standard solution is computed in a similar way. This value, divided by 4 or 5 respectively, gives the time (t_1) required to reach double the viscosity of the standard solution with the same weight of enzyme as in the first experiment. The activity of the enzyme is calculated by substituting in the above equation the values so found. The method, as described above, gives consistent results, with an error of less than 2 per cent. These results are independent of the quality, age or origin of the potato-starch, of the speed of stirring or temperature during the preparation of the starch-paste, of the viscosity of the paste, and of the type of viscometer used. F. A. R.

Changes in the Physical Properties of Regenerated Cellulose by Liquid Ammonia. R. G. Roberts. (*J. Amer. Chem. Soc.*, 1938, **60**, 3084.)—Bags made from regenerated cellulose film placed in liquid ammonia during dialysis of proteins and hormones were observed to change in size and flexibility. Comparative tests were made on the physical properties of the film and ammonia-treated film, by cutting the film into strips, covering it with liquid ammonia (previously dried over metallic sodium) and stoppering and mercury-sealing the flasks. The liquid ammonia had boiled off in about 24 hours and any excess was removed with a vacuum pump. Tear-strength increased 200 per cent.; tensile strength, 70·6; thickness (flat micrometer), 152·4; and weight per unit area, 27·3 per cent.; whilst length (with grain) decreased 8·3 per cent.; width (cross grain), 17·8; area, 24·7 per cent. The ratio of increase of tear-strength to decrease in area was approximately 8 to 1, and increase of tensile strength to decrease in area approximately 3 to 1. D. G. H.

Inorganic

Sulphamic Acid as a Standard in Acidimetry. S. M. J. Butler, G. F. Smith and L. F. Audrieth. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 690–692.)—Sulphamic acid, NH_2SO_3H, is a crystalline non-hygroscopic stable solid (m.p. 205° C. with decomposition). The solubility in 100 g. of water ranges from 14·68 g. at 0° C. to 47·08 g. at 80° C.; the solution does not keep well owing to slow hydrolysis. It is a strong acid and can be titrated with alkalis with the use of indicators over the ranges of *p*H from 4 to 9; the best indicator is bromothymol blue. The results of standardisation tests with baryta were slightly low as compared with constant-boiling hydrochloric acid. This was due to a small trace of occluded moisture in the sulphamic acid which could not be removed by drying. Most sulphamates are soluble in water. S. G. C.

Determination of Redox Potentials with Indicators (*r*H-Measurements). Anon. (*Chem.-Ztg.*, 1938, **62**, 912.)—Redox potentials are analogous to *p*H values, in that they express the potential oxidising or reducing powers of a system and the potential acidity, respectively, irrespective of the actual amounts of the active substances concerned present. They are measured by similar methods, *i.e.* electrometrically, or colorimetrically (by means of indicators), and the following is suggested as a series of indicators covering the entire range of *r*H values and showing their potentials in volts (at *p*H 7) and their *r*H ranges, respectively:—Neutral red, −0·32 and 2 to 4·5; safranine-T, −0·29 and 4 to 7·5; sodium indigo disulphonate −0·11 and 8·5 to 10·5; potassium indigo trisulphonate, −0·07 and 9·5 to 12·0; potassium indigo tetrasulphonate, −0·03 and 11·5 to 13·5; methylene blue, +0·01 and 13·5 to 15·5; thionine, +0·06 and 15 to 17; toluylene blue, +0·11 and 16 to 18; thymol indophenol, +0·18 and 17·5 to 20; *m*-cresol indophenol, +0·21 and 19 to 21·5; 2.6-dichlorophenol indophenol, +0·23 and 20 to 22·5; diphenylamine sulphonic acid, +0·83 (in *N* sulphuric acid) and 27 to 29. Industrial applications are described. The passivity of metals may be related to the *r*H value because metals are attacked by acids only within certain *r*H ranges, and oxidising agents which form protective layers raise the *r*H value; the *r*H values concerned differ according to the nature of the metal and the attacking acid. Aluminium may be regarded as "redox-neutral," whilst iron requires a higher redox potential to produce passivity. The corrosion-inhibiting effects of small quantities of quinone are due to the fact that this substance raises the redox potential of sulphuric acid to +0·33 volt, corresponding with an *r*H value of 11. In connection with the brewing industry, it has been found that enzyme action depends on the *r*H value; a high value is necessary in order that fermentation may proceed, and an optimum value exists for yeast. In order that a beer may be stable, however, a lower *r*H (*e.g.* 9 to 10) is necessary, and this is attained as the result of storage and exclusion of air. The characteristic flavour developed by beer on exposure to a source of strong light is accompanied by a rapid fall in the *r*H value. The formation of many types of beer-turbidity, and particularly those associated with access of air to the beer, is accompanied by changes in *r*H value, and the "cooked" flavour, which sometimes results on pasteurisation, may be avoided if the *r*H value is not allowed to exceed 10. Similarly, with wine, the normal *r*H value of which is 18 to 21 when the wine is in contact with air, although when it is in storage the *r*H value may fall as low as 10. The bouquet of the wine may also be related to the *r*H value.

J. G.

Potentiometric Determination of Mercury with Vanadium Sulphate in Alkaline Solution. C. del Fresno and E. de Lafuente. (*Gazz. Chim. Ital.*, **1938**, **68**, 619–625.)—Quadrivalent vanadium can exist in alkaline solution in the form of five different ions—$V^{\cdot\cdot\cdot\cdot}$, $VO^{\cdot\cdot}$, VO_2, VO_3'', VO_4''''. The oxidation-reduction potential varies inversely with the concentration of the hydroxyl ions, whatever the ionic state of the vanadium.

The potentiometric determination of mercury depends on the reduction of bivalent mercury salts by vanadium sulphate. Potassium iodide was added to the mercury salt solution to form a precipitate which was redissolved in the required quantity of precipitant; the desired quantity of solid sodium hydroxide was then added. The solution thus obtained was titrated with *N*/10 vanadium sulphate solution which was prepared by dissolving 11·750 g. of very pure ammonium vanadate in 27 ml. of pure sulphuric acid (sp.gr. 1·84) and diluting with water to about 500 ml., when the vanadate became red; the solution was brought to the boiling-point and a current of sulphur dioxide was passed through, the vanadate becoming first green and then blue but remaining transparent. The current was stopped, the boiling was continued, and a current of carbon dioxide was passed through to drive off the sulphur dioxide. When the issuing gas did not decolorise a dilute potassium permanganate solution acidified with sulphuric acid the current was stopped, and the liquid was cooled and made up to 1 litre. The concentration of the solution can be checked by potentiometric titration with potassium permanganate solution, which is compared potentiometrically with sodium oxalate. A *N*/10 solution of mercuric chloride was made up by dissolving the theoretical quantity (13·546 g.) of the very pure salt in water and making up to 1 litre. The titration proceeds more quickly and gives better results at 80° to 90° C. than at room temperature.

Because of the ready oxidisability of quadrivalent vanadium in alkaline solution the titration was carried out in a closed vessel in an atmosphere of nitrogen. The wide mouth of the vessel was closed with a rubber stopper through which passed the stirrer (with a mercury seal), a tube for attachment to the burette, this tube ending in a capillary, a T-tube, a syphon containing saturated sodium sulphate solution which connected the vessel with a normal calomel electrode, a thermometer, and an exit tube for the nitrogen; one end of the T-tube served as an entrance tube for the nitrogen, and the other was closed with a rubber stopper carrying a platinum wire, 1 mm. in diameter and 25 cm. long, which acted as the second electrode. Results are presented in a graph and tables which show that the potentiometric determination of mercury by this method can be carried out in the presence of 11·1 and 27·7 per cent. by weight of sodium hydroxide. E. M. P.

Determination of Nickel, Cobalt and Copper in Ores poor in these Metals, by Internal Electrolysis without Diaphragm. J. J. Lourie and L. B. Ginsberg. (*Zav. Lab.*, 1938, **7**, 535–542.)—Nickel and cobalt cannot be deposited by internal electrolysis with iron, cadmium or chromium anodes, owing to the displacement of the potentials of these metals in an ammoniacal medium, but a zinc anode gives good results. A complex fluoride of iron is not decomposed by the current in a weakly ammoniacal medium; hence for the deposition of nickel and cobalt in the presence of tervalent iron the latter must be combined with sodium fluoride. If more than 3 mg. of chromium are present it must be precipitated as barium chromate before the determination of nickel and cobalt, otherwise deposition of these metals is delayed or prevented. Copper, if present, must be removed before the determination of nickel, otherwise it also is deposited when a zinc anode in a weakly acid medium is used. Copper may be determined in a 1 per cent. solution of sulphuric acid, using an iron or aluminium anode. Amounts of iron less than 0·1 g. do not affect the determination of copper; large amounts must be combined with sodium fluoride or reduced with hydrazine. Results for these metals by this method are very accurate for ores poor in them. They agree with those obtained by more elaborate methods. E. B. D.

Precipitation of Nickel and Cobalt Sulphides in a Crystalline State. E. A. Ostroumov. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 693–694.)—Nickel and cobalt sulphides may be precipitated by hydrogen sulphide, from a solution containing pyridine, as a lustrous crystalline precipitate which settles quickly and can be filtered and washed easily. The solution of the cobalt or nickel salt, if acid, is neutralised with sodium carbonate until a turbidity is developed; this is cleared with a few drops of hydrochloric acid. A solution of pyridine hydrochloride (0·5 ml. of hydrochloric acid, sp.gr. 1·12 diluted with 25 ml. of water and neutralised to methyl red with pure pyridine) is added. The solution (150 to 200 ml.) is heated to boiling, 5 to 10 ml. of 20 per cent. aqueous pyridine are added (5 to 6 ml. required for 0·1 g. of nickel or cobalt; moderate excess not objectionable) and hydrogen sulphide is passed to precipitate the sulphide. The precipitate is filtered off and washed with hydrogen sulphide water. Ammonium salts do not interfere.
S. G. C.

Photometric Determination of Cobalt, Iron, and Copper in Nickel Sulphate. T. Somiya and Y. Yasuda. (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 314B–315B.)—Fifty g. of nickel sulphate are dissolved in 100 ml. of water and 12 ml. of 4 *N* sulphuric acid. The solution is gently boiled with 0·5 g. of zinc for half-an-hour, filtered, and the precipitate washed with 0·05 per cent. sulphuric acid. The filtrate is boiled as before with 0·5 g. of solid zinc amalgam and filtered, and the residue is washed as before. The filtrate is treated with more sulphuric acid and the iron is titrated photoelectrically with 0·01 *N* permanganate solution. The zinc and zinc amalgam collected after reduction of the solution are dissolved in 5 ml. of strong nitric acid, the red fumes are expelled by boiling, and the solution is again boiled after addition of 3 ml. of bromine water. A slight excess of ammonia is added, then a slight excess of acetic acid, water to a volume of 100 ml., and 8 g. of potassium iodide. The liberated iodine is titrated photoelectrically with 0·01 *N* thiosulphate. Cobalt is determined in 10 g. of nickel sulphate dissolved in 50 ml. of water, together with 2 g. of sodium pyrophosphate. The air in the flask is displaced by nitrogen, and the solution treated with 5 ml. of strong ammonia and 10 g. of ammonium carbonate. The solution is diluted to 100 ml. and titrated photoelectrically with 0·1 *N* hydrogen peroxide, the cobalt being oxidised to the tervalent state. The end-point is stated to be sharp, but manganese interferes with the cobalt determination. W. R. S.

Determination of Cobalt in Presence of Nickel. D. C. Sen. (*J. Indian Chem. Soc.*, 1938, **15**, 473–474.)—The solution, containing 0·01 to 0·04 g. of cobalt, is diluted to 200 ml., heated to boiling, and treated with 50 ml. of 10 per cent. sodium acetate solution and a 1 per cent. alcoholic solution of iso-nitrosothiocamphor until precipitation is complete. The liquid is well stirred and filtered through a sintered glass crucible. The precipitate is washed with hot water, 0·2 *N* sodium hydroxide solution to remove excess reagent, 2 *N* hydrochloric acid, and finally hot water, dried at 105° to 110° C., and weighed as $(C_{10}H_{14}SNO)_3Co$. It may also be collected on paper, washed with hot water, ignited, and converted into, and weighed as, sulphate. If nickel is present, 30 ml. of 2 *N* hydrochloric acid are added after precipitation, and the solution is allowed to stand for 30 to 40 minutes at room temperature before being filtered. W. R. S.

Volumetric Determination of Cerium by Means of Vanadous Sulphate. P. C. Banerjee. (*J. Indian Chem. Soc.*, 1938, **15**, 475–478.)—Cerous oxalate, either pure or admixed with oxalates of the other rare earths, is heated with strong sulphuric acid in a porcelain basin until white fumes are given off. The solution is oxidised with ammonium persulphate according to von Knorre's directions, cooled, and diluted to 200 ml. with air-free water. Strong sulphuric acid (5 to 10 ml.) and 2 drops of a 1 per cent. solution of diphenylamine in sulphuric acid are added, and the solution is titrated in an atmosphere of carbon dioxide with vanadous sulphate solution until its blue colour is completely discharged. The vanadium solution is standardised against pure ceric sulphate. The titration may also be carried out by adding excess of vanadous sulphate and titrating back with permanganate, the latter being used as a standard for the vanadium solution.

W. R. S.

Determination of "Wetting-out" Agents. R. Hart. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 688–689.)—The wetting-out agents considered are those of the sulphuric acid ester and the sulphonic acid type. The method involves converting them into the ammonium salt having the formula $ROSO_3NH_4$ or RSO_3NH_4 as the case may be (R is an organic group). The ammonium salt, after conversion into ammonium sulphate, is distilled with sodium hydroxide solution in the usual way and the ammonia in the distillate is determined by titration. As from the above formulae one molecule of ammonia is equivalent to one molecule of organically combined sulphur trioxide, the result can conveniently be expressed in terms of percentage of combined sulphur trioxide present in the sample. The conversion of the original compound into the ammonium salt is effected by shaking the solution of the sample in an organic solvent—ether or ether-alcohol mixture—with saturated ammonium chloride solution, the aqueous liquid being rendered just acid to methyl orange with hydrochloric acid. Repeated shaking of the ethereal layer with 5 successive portions of ammonium chloride solution, with intervening separating off, is necessary. The ammonium salt of the sulphonic compound remains in the ether together with a little ammonium chloride. The ethereal layer is then washed similarly with conc. sodium sulphate solution. This decomposes the ammonium salt, changing it into the sodium salt which remains in the ether, while the equivalent amount of ammonium sulphate passes into the water layers, in which the ammonia is determined as referred to above; this ammonia value is somewhat too high, as it includes the ammonia from the ammonium chloride which accompanied the ammonium organic sulphonate salt in the first ethereal solution and passed into the sodium sulphate wash liquid. Correction is made by determining the chloride volumetrically in the usual way and calculating the equivalent amount of ammonia, which is deducted from the ammonia found in the distillate. S. G. C.

Microchemical

Use of Filter Beakers in Organic Halogen Determination. A. Abrahamczik and F. Blümel. (*Mikrochim. Acta*, 1938, 3, 185–189.)—Halogen is determined by the usual micro-Carius method. The mixture is transferred by suction from the bomb-tube to the Jena glass filter-beaker by means of a narrow bent tube of 2 mm. bore, reaching to the bottom of the bomb-tube and bent over to pass through the opening into the filter-beaker. The sintered glass plate of the filter-beaker should be G4 or G4S. By filtering the precipitate in the filter-beaker which is subsequently weighed the determination may be carried out rather more rapidly than by using the Pregl filter tubes containing asbestos. The determination is also more accurate, owing to the absence of asbestos as a filtering medium.

J. W. M.

Test for Cadmium. C. Mahr. (*Mikrochim. Acta*, 1938, 3, 300–303.)—Cadmium may be detected in 0·1 per cent. solutions without previous separation, in the presence of metals of the ammonium sulphide group and the alkaline earths, by the formation of the crystalline compound $Cd(TH)_2[Cr(NH_3)_2(CNS)_4]_2$ (TH = thiourea). By means of a simple separation cadmium may be detected in 0·2 per cent. solutions, in the presence of metals of the hydrochloric acid and hydrogen sulphide groups. *Detail.*—One or two drops of the test solution are evaporated to dryness on a microscope slide, and the residue is dissolved in a small drop of 1·2 *N*-hydrochloric acid and mixed with a large drop of a 1 to 1·5 per cent. solution of Rochelle salt and a drop of a 5 per cent. solution of thiourea. Either at once or after standing for a few minutes, rod-like crystals of the light red cadmium-thiourea tartrate appear, which form clusters and stars. The crystal size varies from 10–40μ according to the time of crystallisation and the concentration of hydrochloric acid, and of the foreign salts present. When interfering elements are present (Groups I and II), the acid test solution is dropped, with stirring, into a mixture of conc. ammonia, hydroxylamine hydrochloride and sodium sulphite (the two latter in 3 to 5 per cent. solutions), and boiled. The mixture is allowed to stand and filtered, and a small portion of the filtrate, which should still be ammoniacal, is acidified with hydrochloric acid and heated. A drop of Rochelle salt solution is added to test for copper; if a yellow precipitate forms the whole filtrate is treated similarly, *i.e.* acidified with hydrochloric acid, treated with Rochelle salt, heated and filtered. In the absence of copper, gold and platinum this stage is omitted. One or two drops of either filtrate are evaporated to dryness on a slide, any excess of ammonium salts are driven off by heating, and the residue is treated as described above for the test in the absence of interfering elements. Lead salts also form crystals under the same conditions, but these are readily distinguishable from the cadmium crystals. J. W. M.

Detection of Zinc with β-Naphthoquinoline and Thiocyanate. E. B. Sandell, D. M. Wishnick and E. L. Wishnick. (*Mikrochim. Acta*, 1938, 3, 204–209.)—The reagent solution is prepared by adding a 5 or 10 per cent. solution of potassium thiocyanate to a 1 per cent. solution of β-naphthoquinoline in 0·1 *N*-sulphuric acid until a slight permanent turbidity appears. Characteristic crystals of zinc hydrogen β-naphthoquinoline thiocyanate are obtained in 2 *N*-sulphuric acid solution with zinc concentrations as low as 1 : 200,000. The test can be carried out in the presence of moderate amounts of calcium, magnesium, beryllium, aluminium, tervalent chromium, tervalent cerium, ter- or quinquevalent arsenic, manganese and nickel as well as of the alkali metals. If the reagent is prepared with acetic instead of sulphuric acid it gives no precipitate with barium, and with lead no immediate precipitate separates, but long prismatic crystals are formed later. Zinc in 1 : 100,000 concentration can be detected in presence of any of these metals except lead. Cadmium in concentrations below 0·5 per cent. does not interfere; ferric iron in amounts up to 1 per cent. does not interfere if the test is carried out in 50 per cent. phosphoric acid solution. Most other metals give precipitates with the reagent. J. W. M.

Physical Methods, Apparatus, etc.

Measurement of the Temperature in Certain Industrial Processes. Anon. (*Chem.-Ztg.*, 1938, 62, 932.)—The method described is recommended for the measurement of the temperatures reached in inaccessible portions of an object, and it eliminates the expense and inconvenience of thermo-elements. It was evolved to measure the temperatures reached inside wooden objects during the process of impregnation with coal-tar oils under pressure at a high temperature. For this purpose holes were bored at suitable places, and in them were inserted cylindrical metal capsules (length 20 mm., diameter 7 mm.). Each capsule was provided with a wire loop to aid removal after the impregnation process, and it contained 12 sealed melting-point tubes (length 15 mm., diameter 1 mm.), each of which contained one of the following substances having the melting-points stated, in °C.:—Azoxy-benzene, 37°; salol, 43°; α-naphthylamine, 48°; diphenylamine, 55°; benzoyl acetone, 59°; β-naphthonitrile, 65°; coumarin, 71°; *o*-hydroxy quinoline, 75°; naphthalene, 81°; 3.5-dinitro-*o*-cresol, 86°; *m*-dinitrobenzene, 90°; and *m*-nitrophenol, 95°. The hole was closed with a wooden block and, after the processing, the capsules were removed. The temperature required could then be obtained from the mean of the m.p. of the substance having the highest m.p. in the series and which had melted, and of that of the substance having the lowest m.p. of the series which had not melted. In this way any desired range of temperatures may be covered, so long as the substances chosen melt sharply and show a visible difference in appearance after they have done so. J. G.

Micro-structure and Diffraction Pattern of Basswood Ash. E. A. Parker, W. E. Patzer and G. J. Ritter. (*J. Amer. Chem. Soc.*, 1938, **60**, 2980–2982.)—Ash residues were prepared from basswood cross sections for determining the micro-structure of the ash and the location of the ash-forming constituents, and also from small wood cubes for comparing its crystalline arrangement with that of ash from sawdust. The residues form intact skeletons of the wood. This was made possible by using an electric furnace with a carefully controlled current of oxygen and ozone. The thin wood sections were mounted on glass slides in a drop of a medium consisting of equal parts of ash-free linseed oil and turpentine, previously hardened at room temperature in a current of oxygen and ozone. With the transverse sections the walls are thinner, and as a lateral shrinkage of the ash-cell occurs, the ash in the secondary layer is drawn towards the middle lamella. Occasional interruptions occur between two adjacent cell-walls of the ash; these are regarded as entirely due to the sectioning of the wood. The ash-forming minerals in wood are present both in the cell-wall and the middle lamella. In order to study the crystal arrangement of the ash obtained from wood cubes of 3 mm. edge a photographic pattern was made by passing an X-ray beam through the block perpendicularly to the long axis of the fibres. The diffraction pattern recorded on a flat film indicated random arrangement of the ash crystals, just as in the ash of sawdust from the same wood. By a comparison of the diffraction pattern of the ash with those of known compounds, it is shown that the only visible diffraction lines are produced by the carbonate and oxide of calcium.

D. G. H.

Errata.—DETERMINATION OF DISSOLVED OXYGEN IN CONDENSED STEAM (January issue, p. 66).—The figures on line 23 *should read*:—0, 0·05, 0·001; 0, 0·34, 0·005; 0·95, 0·69, 0·01; 1·89, 1·90, 0·03; 1·92, 3·14, 0·05.

Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. By J. F. THORPE, C.B.E., D.Sc., F.R.S., and M. A. WHITELEY, O.B.E., D.Sc., F.I.C. Fourth Edition. Vol. II: B—Chemical Analysis. Pp. 711. London: Longmans, Green & Co. 1938. Price 63s.

This volume includes parts of Volumes I and II of the last edition, but it cannot be compared strictly with its predecessors because of re-arrangements of subject matter in accordance with the scheme outlined in Volume I (to which reference was made in a review of that volume, ANALYST, 1937, **62**, 907).

It has been suggested sometimes that the Dictionary devotes too much space to organic chemistry but, as pointed out in the preface, this criticism is based upon optical illusion. The formulae are necessarily spacious and so articles involving organic compounds are apt to appear long, whereas in fact a greater amount of reading matter is devoted to inorganic and physical chemistry. In the reviewer's opinion the articles connected with organic chemistry are specially excellent because of the lucid way in which difficult subjects are explained. Those whose organic chemistry is less facile than it once was will find admirable summaries under the various headings in this volume. Moreover, there is an abundance of references, so that, having carefully read the article, one is in a position to refer to original memoirs more easily and with greater profit. The authors have given us a number of monographs on fundamental matters which are calculated to throw light on some of the more strictly industrial topics. It appears, therefore, that they have held the balance between pure and applied chemistry with much skill.

Consideration of the details of some of the more important articles gives the impression that the work has been very well done. It is almost invariably up-to-date and one cannot but be struck with the clarity with which quite difficult matters are summarised. Perhaps this may be illustrated by reference to an article of particular interest to readers of THE ANALYST, *viz.* that on Analysis. This topic disappeared from Volume I, to re-appear in an extended form in Volume II, under the heading "Chemical Analysis." It is from the versatile pen of Sir Gilbert Morgan with parts by Dr. G. A. R. Kon, Dr. Drew and others, and occupies 170 pages. If an author wrote a book on chemical analysis in 170 pages, it would doubtless be thought to be somewhat inadequate for so wide a subject. Nevertheless, when one peruses this article it is difficult to find any fundamental analytical operation which is not mentioned. Most of us have several books on qualitative analysis including group separations; these usually omit from their schemes the less common elements such as tellurium, rhenium, zirconium, hafnium and the like; but almost all the metals are included in the tables here given, and that without making them unduly bulky. The special reactions and organic reagents for metals, including less common ones, are given, and tests for the more frequently occurring acid radicals. There are also sections on chromatographic analysis, micro-chemical analysis, spectrographic analysis and gas analysis. The authors and editors are to be congratulated on this important section of the volume.

Many new headings have been noted; one on Building Materials. This is largely new and deals with bricks, clay products, lime, stone, magnesium oxy-chloride cements and so forth, and covers in an abbreviated form the old article on Portland Cement. The range of topics included may perhaps be indicated by jumping from Building Materials and Butter to Carcinogenic Hydrocarbons (by Dr. Quastel). In mentioning butter an omission is noted, in that the description of the Reichert–Meissl process follows the details laid down in 1911 rather than the now standardised Reichert–Polenske–Kirschner procedure.

The article on Carbohydrates may be mentioned because, while it presents the more recent advances in this subject, it has been successfully condensed so that it now occupies 20 pages instead of 30.

More information is given on Carbon Disulphide, as is appropriate to its increased industrial use. Indeed, throughout the work the authors seem to have skilfully gauged the length of their articles in relation to industrial importance.

The type and make-up of the volume are in the familiar form, and formulae have been very clearly set out. Few printer's errors have been noted, and the whole volume well maintains the high standard of its predecessors. It will be acquired by analysts as a matter of course. H. E. Cox

THE EXTRA PHARMACOPOEIA. (MARTINDALE.) Volume II. Pp. xxxvi + 1040, and Index, p. 107. London: The Pharmaceutical Press. 1938. Price 22s. 6d.

The twenty-first edition of *Martindale*, like its six predecessors, has been published in two volumes, and during the fifty years in which this work has become indispensable alike to medical practitioners and pharmacists, it has grown from a small volume of 313 pages to two of a somewhat larger size, comprising in all 2330 pages.

The value of the book cannot be assessed in terms of pages; since the first volume was issued, the changes in medicine and pharmacy, and consequently in analytical chemistry, have been epoch-making. William Martindale saw the introduction into medicine of the synthetic drugs and chemicals—such substances as antipyrine, saccharin and vaseline—and lived until bacteriology and radiology became recognised sciences. During the lifetime of his son, Dr. W. H. Martindale, who continued as the author, the world became flooded with synthetic remedies, and with proprietary medicines, whose names are now household words, and the discovery of vitamins, the uses of radium, thyroid, adrenaline and pituitary, and the thousand and one new applications of chemical substances to medical practice have necessitated a special literature.

After the decease of the younger Martindale, the Pharmaceutical Society resolved that the book should not be allowed to lapse for want of an author, and the Council of the Society and a special Revision Committee are now responsible for the revision and production of a book which has become a classic.

Of necessity, these changes in medical practice have introduced new methods of technique in the application of new remedies, entirely fresh aids to the diagnosis of disease, and absolutely different biological factors which call for analytical control in ways undreamed of half a century ago. These are all recorded in this new Volume II of *Martindale*, and it is impossible to find any published work of significance which has not been abstracted and included in it. When the numerous current medical and chemical publications have to be perused weekly or periodically, to keep in touch with modern practice, it becomes necessary to have a reliable resumé for consultation, and despite the rapid changes which are inevitable, it is safe to assert that there is no more up-to-date book than this published in the English language dealing with these kindred subjects.

The volume opens with 332 pages of Analytical Addenda to Materia Medica, which includes the methods of analysis of the drugs officially recognised by the British Pharmacopoeia, and a very large number of their preparations as well as many of those which are as official as their inclusion in the British Pharmaceutical Codex can render them. This section of the book will be of great assistance to practising analysts; it includes details of many of the British Standard Specifications.

The portions dealing with vegetable drugs and their assay are as up-to-date as the time taken for publication will allow, and the pages devoted to fixed and essential oils include all the more recent work on these most important items.

Following these is a section of 47 pages dealing with Proprietary Medicines, which provides the published formulae of most of the preparations met with in medical practice, or commonly used by the public at the present time. Then the book delves deeply into organic chemistry, with a most informative chapter on the Nomenclature of Organic Compounds, which gives the graphic configuration of the homocyclic, alicyclic and heterocyclic and other compounds whose composition can be comprehended better by these graphic descriptions than by stringing together the names of the chemical radicals of so many of the complicated substances now in constant employment in medicine.

Chapters on the action of acids on metals and oxides, organic reagents for inorganic analysis and a Scheme for the Recognition of Organic Chemical substances used in therapeutics, and a chart of corroborative tests for 331 organic substances make up a section of the book which every analyst will want to possess if his work lies in that field.

Hydrogen Ion Concentration, Indicators, Fluorescence Analysis in Ultraviolet Light, and Chromatographic and Microchemical Analysis are all dealt with in a very helpful manner.

One of the particularly useful portions of the book is concerned with the Chemical Tests and Microscopic methods for testing Urine, Blood, Faeces and Stomach-contents, and this is followed by chapters on Nutrition and on Vitamins.

Another chapter deals most effectively with the analytical information and the laws controlling the sale of Milk and Milk Products, and necessarily also with the analysis of dairy products, and with the Food and Drugs Act Regulations and the Ministry of Health Regulations now in force. Butter and Jam Analysis, Food Preservatives, and Dyes used in Colouring Food have been very effectively presented.

Quite a large section of the volume is devoted to Bacteriological and Clinical Notes, and this is almost a compendium for the use of a general medical practitioner, for it deals clinically with most of the endemic and epidemic diseases, and their method of treatment by the latest published methods.

Radium, X-ray Therapy, and Electrotherapy, as well as the uses of Ultraviolet Light are considered at length with very numerous references to published results.

Glossaries of terms used in medicine and pharmacy will be found useful for workers needing Dutch, French, German, Italian, and Spanish translations.

Although so much of value is included in the book, yet the 107 double-column pages of index can be singled out for special mention; the text without such a comprehensive compilation would lose so much of its usefulness that special praise can be offered for the care given to this portion of a most valuable volume.

The reviewer's work has required constant reference to a dictionary of medical terms, and for the benefit of future users of *Martindale*, it may be possible to add a glossary of such terms. The ever-growing field of medicine and surgery is constantly adding to a vocabulary which is already unwieldy, and the need for some such shortened dictionary of medical terms might well be considered by the Society that has published this 21st edition of an essential companion for the works in a public analyst's library. C. EDWARD SAGE

FOOD AND HEALTH. By A. BARBARA CALLOW. 2nd Edition. Pp. ix+168. Oxford University Press. 1938. Price 5s.

This is certainly the volume to recommend to the general reader who wishes to get a simple and concise account of modern views on nutrition and human diet. Ten years is a long time in a field of research in which progress is as rapid as it is in experimental nutrition. It is not surprising, therefore, that Mrs. Callow has found it necessary almost completely to re-write a work which first appeared in 1928. The result is in every way admirable. In simple language and with well chosen examples and illustrations she gives an account of modern views on the requirements of the human body.

Many of the tables which the book contains are of a very useful type. Thus, for example, in addition to the conventional tables giving the composition of various foods, Mrs. Callow gives lists showing the amounts of certain foodstuffs which provide the daily requirements for particular nutrients, such as the more important vitamins.

The volume is well produced and commendably free from error. In the table on page 141, "Marmite" is stated on the authority of the manufacturers' analyses to contain 3000 International Units of vitamin B_1 per gramme. Possibly this is a misprint, but if not it would be interesting to have details of the assay, as this value is about ten times that usually accepted.

The author is to be congratulated on having carried out a difficult task with skill and discretion. J. C. DRUMMOND

AN INTRODUCTION TO THE CHEMISTRY OF CELLULOSE. By J. T. MARSH, M.Sc., and F. C. WOOD, Ph.D., F.I.C. Pp. xv + 431. London: Chapman & Hall. 1938. Price 21s. net.

In the past few years a very large number of papers have been published dealing with the inter-related subjects which can be grouped under the heading "Cellulose Chemistry." It has therefore become increasingly difficult to obtain and maintain a general view of the whole subject, and the present volume should be very useful for this purpose.

The work has been divided into five sections, covering general properties, dispersed and modified celluloses, derivatives, and molecular structure, and each is dealt with in very great detail.

The encyclopaedic method adopted often prevents or obscures the selection which is so valuable in guiding students new to the subject, but it of course increases the value of the book to the established worker in the field. Actually, this must be regarded as a guide-book rather than an "Introduction" to cellulose chemistry, and indeed the authors also appear to be of this opinion, as indicated by their preface.

Because of the predominance of the textile industry in this country, it has become general to regard cellulose chemistry as concerned only with textile materials, to the exclusion of the wood pulp and paper industries. Thus, the vexed question of "hydration," which has been one of the principal problems of the workers in the paper field, is here discussed from the point of view of "textile" chemists only.

Apart from some passing references, the whole of the wood-pulping industry is dismissed in two lines on page 329, and, incidentally, the reference which immediately follows is incorrect, and should read "*Journal of the Textile Industry*, 1936, **27**, 169."

These are, however, relatively small matters when compared with the general excellence of the book, which makes it a very useful guide to the subject.

L. G. S. HEBBS

A TEXT-BOOK OF INORGANIC CHEMISTRY. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Vol. VI, Part IV: ARSENIC. By REECE H. VALLANCE, M.Sc., F.I.C. Pp. xxxi + 351. London: Charles Griffin & Co., Ltd. 1938. Price 25s.

This work—the fourth in Dr. Friend's series—is a detailed and carefully compiled monograph on the present state of our knowledge of arsenic. The subdivision into chapters is as follows:—Occurrence; Properties; Metallic Arsenides; Hydrides; Halides; Lower Oxides and the Arsenites; Pentoxide and Arsenates; Sulphides; Physiological Properties; Arsenical Sprays and Dusts; Detection and Estimation. The arsenites and arsenates of the metallic elements are described in alphabetical order, a very convenient arrangement; and the amount of detail may be judged from the fact that the metallic arsenates occupy 46 pages of print. Eighteen pages are devoted to the study of colloidal arsenic sulphide alone. The analytical chapter (18 pages) is short in comparison, but reliable and informative, and supplemented by copious references. The author has evidently spared no pains to compile a comprehensive up-to-date reference book on the subject.

It may be somewhat startling to many of us to read that a newcomer amongst arsenic producers (the Boliden refinery, N. Sweden) has an annual output of 40,000 tons of white arsenic, more than the world's requirements, the surplus having to be stored in huge concrete containers; and that more than 70 per cent.

of this production is disseminated over the earth's surface in an endeavour to combat plant and animal pests, a problem requiring expert control.

The proof-reading has been done with the greatest care, and only one or two minor misprints have been noticed.

An addendum to the General Preface states that the present volume completes the original scheme for this series of text-books, and that a revision of the earlier volumes has begun. This will, it is hoped, result in the publication of separate books for a number of elements, the original plan of devoting only one book to each group in the Periodic Classification having been followed in only three instances.

W. R. SCHOELLER

BREWING SCIENCE AND PRACTICE. Vol. I: BREWING MATERIALS. By H. LLOYD HIND, B.Sc., F.I.C. Pp. xiv + 505, with 63 illustrations. London: Chapman & Hall. 1938. Price 50s. net.

For many years there has existed a pressing need for a volume or series of volumes dealing comprehensively with the malting and brewing industries and including the scientific principles upon which these are based as elucidated by the intensive investigations carried out during the last few decades. With the object of providing such a work the author has undertaken the arduous task of summarising and correlating the widely-spread literature of both the practical and scientific aspects of this complex craft, and the present volume is devoted to the materials used in brewing, whilst Volume II, to be published shortly, will deal with the brewery processes in which they are used.

The text opens with a description and illustrations of an interesting old-world relic—the brewery at Queen's College, Oxford, in which the famous college ale has been brewed since the year 1340; this is followed by a brief history of the science underlying the art of brewing in general and culminating in the brilliant researches of Pasteur, Hansen and Buchner. The four following chapters are devoted to barley and provide detailed information of the numerous varieties, their structural and physiological characters, composition, assessment of brewing value and prediction of the extract they will yield when converted into malt. At first sight the next division would appear to be misplaced, since it deals with physical chemistry and biochemistry and their application to malts and worts, but without this preliminary account of colloids, hydrogen ion concentration, enzymes, and so forth, the following five sections, relating to malting and the various classes of malt, would be difficult to follow. The remaining 200 pages of the volume are devoted to sugars, hops and water, their sources, varieties, uses, treatment and suitability for different types of beer being described in full detail. The whole subject is envisaged from the aspects of both the brewer and the scientist, and whilst the former may feel that some of his cherished beliefs are being rudely shattered, he will not fail to appreciate that only by the application of scientific method to his industry can be ascertained the reliable facts upon which future progress depends.

Each chapter of the volume is provided with an admirable summary of its contents together with a bibliography to which numerical references are given in the text, but it is unfortunate that the references to other parts of the text are not given with greater precision. For example, "Table M" may be 2, 20 or 200 pages further on, and unless the number of the page is given also, the reader will waste valuable time in the search for an item. A prominent feature of this work is the inclusion of analytical and other results obtained by Continental and American investigators, and the correlation of these with researches carried out in this country. The famous "nitrogen question" of barleys and malts, around which in the past so much speculation and controversy has raged, has at last reached a more rational stage based upon definite knowledge acquired during recent investigations. At the same time it yet remains to be proved whether the ratio of the total nitrogen to the permanently soluble nitrogen, for which the author appears to be an enthusiast, will prove any more trustworthy as an indication of malt modification than other criteria that have been adopted and abandoned in the past.

An unusual feature of the work, and one that is not likely to meet with the favour of readers, is the numbering of the pages in the upper outer corners with that of the section they bear instead of the usual page numbers. As a result of this arrangement three or more pages may bear the same number, whilst other numbers are omitted altogether. As these figures are also given in the index, the actual page numbers placed at the bottom of each would appear to be redundant.

Much care has been expended in the production of this book, with the result that very few errors are evident, although a few inconsistencies occur. Thus, chemists would be interested to know the method by which 0·0111 per cent. of tannin can be estimated so precisely in wort, as given on p. 207. Further, the varietal constants of Spratt–Archer and Plumage–Archer barleys are given as 108·9 and 108·3, respectively, on p. 91, but elsewhere these values are stated to be 108·5 and 108·0. Similarly, with regard to water hardness on p. 429 a "hard" water is defined as one containing an equivalent of 25 to 35 grains per gallon of *calcium carbonate*, but the same designation is used on p. 457 for one containing 14 grains per gallon of *total solids*.

These minor defects, however, detract but little from the value of the work, which is written in excellent English with a lucidity and interest often missing from the original papers used as sources of information, and considerable acumen has been shown in assessing the value of these and rejecting the chaff. The numerous illustrations, whether produced from photographs or drawings, are excellent in every way, and the volume is completed by the usual name and subject indexes, both of which show a high degree of accuracy, although the latter, while extensive, still omits some minor items deserving inclusion in the text.

Both the author and the publishers are to be congratulated on the success they have achieved in the production of this monumental volume, which will prove invaluable both as a textbook and a work of reference to all connected with the brewing industry whether as maltsters, brewers or chemists. In particular, it will save the student of brewing much valuable time and trouble in the acquisition of knowledge relating to the science and practice of his profession.

T. J. Ward

THE PHARMACEUTICAL POCKET BOOK. Thirteenth Edition. Published by direction of the Council of the Pharmaceutical Society of Great Britain. Pp. x + 370. London: The Pharmaceutical Press. 1938. Price 5s.

This edition, like the last, published in 1933, has been produced under the supervision of the Codex Revision Committee of the Pharmaceutical Society. Though in the preface it is stated that the reader is assumed to possess the British Pharmacopoeia, 1932, and the British Pharmaceutical Codex, 1934, much of the matter contained in those two books is here reproduced in tabular form, and is thus very convenient for reference. For example, there are tables of The Proportions of Active Ingredients in B.P. Preparations, the Doses of Official Medicaments, and the Materia Medica of Vegetable and Animal Origin. Other useful tables include the specific gravities of many chemicals and other substances, solubilities of most of the substances mentioned in the B.P., in water, alcohol, chloroform, glycerin, and oils, medicinal and fatal doses of poisons, and a veterinary posological table. There is also a very full summary of the Pharmacy and Poisons Act, 1933, together with the Poisons Rules, 1935, as amended by the Poisons (Amendment) Rules, 1937, followed by a chapter on poisons, their symptoms and antidotes.

Whilst of course intended primarily for the pharmacist, the book contains much of direct interest to the analyst, including as it does sections on milk and milk products, food and diet, the vitamins, water analysis, the analysis of blood, of gastric contents, and of urine and urinary calculi, followed by notes on bacteriology and a useful bacteriological chart. Other sections deal with the endocrine organs, the making of a herbarium, and the removal of various stains from cloth or the skin, and the work concludes with a Dictionary of Synonyms, covering 78 pages.

The book is a model of condensation without superficiality, and it is amazing how much information has been included in such a comparatively small volume, and published at such a low price.

As was only to be expected in a book published under such authoritative revision, there is little in its contents which calls for criticism. It is rather surprising under water analysis to find iron classed as a poisonous metal, the quantity of which should not exceed 0·3 part per million, as compared with a maximum limit for zinc of 5 parts. Under Materia Medica olive oil is said to contain "olein, with small amounts of palmitin, linolein and arachin," a statement which omits any reference to the appreciable amount of stearic acid present, and does not take into account the considerable amount of mixed glycerides found in olive oil by Prof. Hilditch. In the Dictionary of Synonyms, gingergrass oil is quite wrongly described as an inferior oil of palmarosa, whereas it is distilled from an entirely different grass. Castile soap is unfortunately no longer synonymous with olive oil soap, and lanette wax is not cetyl alcohol, but a mixture of cetyl and stearyl alcohols, obtained by hydrogenation of commercial stearine, *i.e.* a mixture of palmitic and stearic acids.

W. H. SIMMONS

Publications Received

TEXT BOOK OF ORGANIC CHEMISTRY. By G. HOLMES RICHTER. Pp. viii + 711. London: Chapman & Hall. 1938. Price 20s. net.

INTRODUCTION TO CHEMICAL ANALYSIS. By W. C. VOSBURGH. Pp. vii + 222. London: Macmillan & Co. 1938. Price 10s. net.

QUALITATIVE CHEMICAL ANALYSIS. By L. J. CURTMAN. Pp. xii + 514. New York: The Macmillan Co. 1938. Price $3.75 net.

THEORETICAL CHEMICAL ANALYSIS. By J. H. READY. Pp. ix + 451. London: McGraw Hill Publishing Co. 1939. Price 18s.

HANDBOOK OF CHEMICAL MICROSCOPY. By E. M. CHARNOT and C. W. MASON. Vol. I. 2nd Ed. Pp. xvi + 478. New York: Wiley; London: Chapman & Hall. 1938. Price 22s. 6d. net.

THE MICROSCOPICAL STUDY OF DRUGS. By J. A. KAY. Pp. viii + 228, 47 plates. London: Baillière, Tindall & Cox. 1938. Price 10s. 6d.

AIDS TO FORENSIC MEDICINE AND TOXICOLOGY. By J. H. RYFFEL. 11th Ed. Pp. x + 170. Price 3s. 6d.

NOTES ON PROCEDURE IN FORENSIC CASES INVOLVING LABORATORY EXAMINATION. Tanganyika Territory Medical Department. 1938.

TEXT-BOOK OF PHARMACOGNOSY. By G. E. TREASE. 3rd Ed. Pp. x + 740. London: Baillière, Tindall & Cox. 1938. Price 21s.

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MARCH, 1939 Vol. 64, No. 756

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry was held on Wednesday, February 1st, at 8 p.m., in the Chemical Society's Rooms, Burlington House. At the invitation of Dr. E. B. Hughes, Vice-Chairman of the Food Group, Professor W. H. Roberts, President of the Society, occupied the chair.

The following were elected members of the Society:—G. Carter, B.Sc., A.I.C.; O. B. Darbishire, B.Sc., A.R.C.S., D.I.C., A.I.C.; F. M. Dyke, B.Sc., F.I.C.; A. A. Eldridge, B.Sc., F.I.C.; Professor F. Feigl, Dr.Ing.; G. H. Fraser; M. B. Ichaporia, M.Sc., Ph.D., A.I.C.; R. Porter; A. C. Ratcliff, B.Sc.; W. H. Templeton, B.Sc., F.I.C.

Certificates were read in favour of the following Candidates for Membership:—F. C. Collins; R. Crosbie-Oates, B.Sc., F.I.C.; Prof. H. E. Fierz-David; J. G. Fife, M.Sc., F.I.C.; W. C. Hughes; N. E. G. Narayan Iyengar; W. E. Kemp; H. C. Lockwood, B.Sc., F.I.C.; W. Marsden; F. Michel, Dr.Chem.; A. H. Rheinlander, M.Sc., F.I.C.; L. W. Ruddle; J. Straub, Chem.Ing.; R. G. Thin, B.Sc., F.I.C.; H. Wilkinson, B.Sc., Ph.D.; E. G. Williams, M.A., A.I.C.; F. R. Williams, Ph.D., B.Sc., A.I.C.

The subject dealt with at the meeting was:—"The Analysis and Differentiation of the Composition of Iron, Phosphorus and Calcium Compounds in respect of Nutritional Requirements." The subject was introduced by Professor J. C. Drummond, M.C., D.Sc., F.I.C.; Iron Compounds were dealt with by Dr. R. A. McCance, M.A., M.D., M.R.C.P., M.R.C.S.; Phosphorus Compounds by Professor H. D. Kay, O.B.E., D.Sc.; Calcium Compounds by Professor E. C. Dodds, M.V.O., D.Sc., M.D., F.R.C.P., and Dr. J. D. Robertson, M.D., D.P.H., Ch.B.

NORTH OF ENGLAND SECTION

THE Fourteenth Annual General Meeting of the Section was held at Manchester on January 28th, 1939. The Chairman, Professor T. P. Hilditch, presided over an attendance of thirty-seven.

An appreciation of the late Dr. J. T. Dunn was given by Mr. W. G. Carey, F.I.C., and afterwards, at the request of the Chairman, the members stood in silence as a mark of respect.

The Secretary presented the Report and Financial Statement, which were adopted.

The following appointments for the coming year were made:—*Chairman*, Professor T. P. Hilditch; *Vice-Chairman*, J. R. Stubbs; *Committee*, W. G. Carey, E. G. Jones, A. Lees, H. M. Mason, C. J. H. Stock, A. R. Tankard; *Honorary Auditors*, U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer*, J. R. Stubbs.

The Chairman delivered the Annual Address entitled "Speed Limits in Analytical Matters."

The following paper was read and discussed:—"On the Composition and Analysis of Hair Dyes," by H. E. Cox, D.Sc., Ph.D., F.I.C.

SCOTTISH SECTION

The Fourth Annual General Meeting of the Section was held in the Ca'doro Restaurant, Union Street, Glasgow, on January 26th, 1939.

The Secretary read the Report and Financial Statement for 1938, which were adopted.

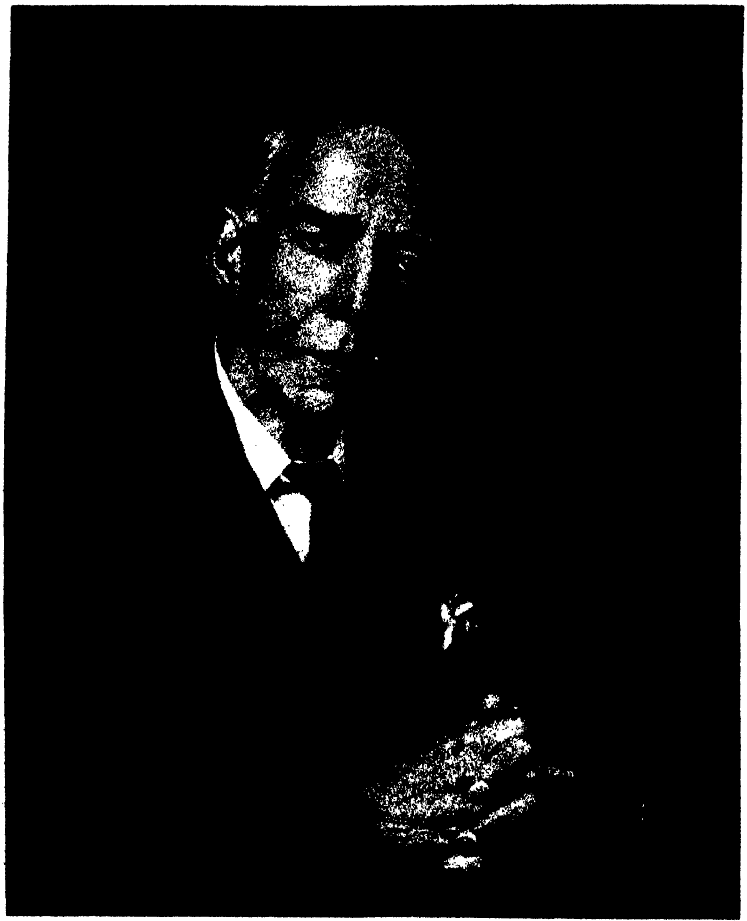
The following office-bearers were elected:—*Chairman*, T. Cockburn; *Vice-Chairman*, J. W. Hawley; *Committee*, J. Brown, H. Dryerre, A. R. Jamieson, H. C. Moir, A. Scott Dodd, J. F. Tocher; *Honorary Secretary and Treasurer*, J. B. McKean; *Honorary Auditors*, M. Herd and R. S. Watson.

The following papers were then read and discussed:—"Sampling," by W. M. Cameron; "Seasoning Materials," by R. H. McKinlay, F.I.C.

After some discussion, the meeting unanimously decided that a Food and Drugs Act applicable to Scotland, on similar lines to the Food and Drugs Act, 1938, was desirable. The Chairman and Secretary were instructed to draft a Memorandum on this subject and to submit it, if approved by the Council, to the Local Government and Public Health Consolidation (Scotland) Committee.

Death

With great regret we record the death of Mr. D. Lloyd Howard, former Member of Council.



Elliott & Fry photographers　　Emery Walker Ph. sc.

J. J. Dunn

Obituary

JOHN THOMAS DUNN

DR. J. T. DUNN died, in his 81st year, in Newcastle upon Tyne, on January 3rd.

The service at the West End Crematorium, Newcastle, on January 6th, was attended by a numerous congregation, representative of his scientific, public, social, cultural and other activities. It was conducted by the Rev. Herbert Barnes of the Church of the Divine Unity, who gave a short address of consolation and an appreciation of Dr. Dunn's attainments and services and of his many-sided character.

This Society was represented by Mr. John Evans, Past President, and other members attending were Messrs. W. Gordon Carey (Sunderland), A. Scholes (representing Pattinson & Stead, Middlesbrough), C. J. H. Stock (Darlington), and H. C. L. Bloxam (Newcastle).

A memorial service was held on Sunday, January 8th, in the Church of the Divine Unity, Newcastle, where Dr. Dunn attended after he came to live in Newcastle. An eloquent address was delivered by Lord Eustace Percy, Rector of King's College, Newcastle, in which he referred to the long and valuable services of Dr. Dunn to the Council of the College.

Dunn was educated at Dr. Bruce's School and at Durham College of Science, later Armstrong College (now King's College), Newcastle. He graduated B.Sc. in 1877 and proceeded to M.Sc. and D.Sc. At Armstrong College he was Demonstrator in Chemistry and Physics and, later, Acting Professor of Chemistry (1882). He then turned to scholastic work, becoming science master at Gateshead School in 1884, and Head Master in 1887. In 1894 he became Head of the Technical School, Plymouth, and in 1895 Principal of the Northern Polytechnic Institute, London, where he was also Head of the Chemistry Department. In 1901 he joined John Pattinson in partnership in the firm of J. & H. S. Pattinson, Analytical and Consulting Chemists, Newcastle upon Tyne, of which he was the senior partner at the time of his death. On Pattinson's death Dunn became Public Analyst for the City and County of Newcastle upon Tyne, the County of Northumberland, the County Boroughs of Gateshead, South Shields, Sunderland, and Tynemouth, and the Borough of Berwick-upon-Tweed; these appointments he held until 1937, when, owing to his illness, his partner was appointed to them.

Dunn was elected a Member of this Society in 1905, served three periods as Member of Council, was Vice-President in 1917–18, and was elected President in 1930. He was President of the Society of Chemical Industry in 1933–4, and was a Member of Council of the Institute of Chemistry, 1918–21, and Examiner from 1921 to 1925 and from 1927 to 1932.

An eminent man has gone from us, but his example remains, and fortunately the many who came in contact with him during his early scholastic and university life, and later in his numerous public and professional activities, have had the opportunity to profit by it. A cultured and scholarly man, of a quiet and kindly disposition, tolerant of the views of others, yet ever ready stoutly to defend his own opinions with a vigour that surprised those who were unacquainted with the depths of his character. He was a fluent extempore speaker, but nevertheless he wrote all important speeches, which he committed to memory and delivered with scarcely a reference to his notes. Of his own language he was a perfect master, and he derived much entertainment from journalese; he possessed an intimate knowledge of French and German, a working acquaintance with Italian, and for business purposes he even made a study of Russian.

As might be expected, he was a scholarly writer, and his manuscript and letters will long be remembered for his choice of words, beauty of handwriting and neat arrangement. Dunn accomplished so much because of his great powers of endurance (he was only once known to admit feeling tired) and because he permitted himself no idle moments; having a few minutes to spare before keeping an appointment or catching a train, he would employ them by writing a short letter, or in making a microscope examination, arriving without hurry, to catch the train almost at the due time for departure. He was never bored, nor did he feel the need of hobbies. Habitually he acted upon the injunction "do it now," rarely delaying or postponing, and no sooner was he asked to do something than he at once set about doing it, if he approved of the request. This characteristic sometimes led to wild searches in the waste-paper basket for a document or letter which, having been at once attended to, had been thrown away, but which, on second thoughts, he wished to file or to refer to again.

Dunn took a deep interest in Rotary, regularly attending the Friday lunches of the Newcastle Club, of which he was a Past President, and he often visited the Rotary Clubs in the neighbourhood of Newcastle; in 1928 he represented Newcastle Rotarians at the International Conference at Minneapolis, U.S.A. He never used the much-hackneyed word "service," yet he was ever ready to do a service for those who needed it; though charitable, he preferred to act through some organisation whose business it was to investigate cases of need. He had a great love of animals, particularly of dogs, and was Secretary and Treasurer of the Newcastle Dog and Cat Shelter, and a member of the Committee of the Newcastle Branch of the R.S.P.C.A. A lover of music, and no mean performer on the pianoforte, he was an active supporter of local music societies, and acted as Local Representative of the Associated Board of the Royal Schools of Music, London.

Dunn was a Justice of the Peace for Gateshead, a Freeman of the City of Newcastle, a member of the Freemen's Guild, and a member of the Ancient Company of House Carpenters, of which he was Senior Steward.

His was a crowded life, yet nothing appeared too great or too trivial to merit his attention, and in all he undertook he gave of his best. Although he passed the normal span of life, he never went through the period of old age, and thus we shall continue to remember him—a man of great activity and usefulness.

He leaves a widow and an only child, Mrs. V. A. Mundella.

H. CHARLES L. BLOXAM

Selective Oxidation of Animal and Vegetable Fats: A New Constant

By W. A. ALEXANDER, B.Sc., A.I.C.

(*Read at the Meeting, December* 7, 1938)

INTRODUCTION.—In this work an attempt is made to utilise selective oxidation as a means of determining the purity of an animal or vegetable fat. Conditions were established under which the amount of oxidation of the more highly unsaturated acids was far greater than that of the less unsaturated, and the difference between them constant and measurable. Thus a "constant" was found which depended largely on the relative proportions of the unsaturated acid components of the fat, as well as on their total amount. The only other method achieving this end would seem to be the thiocyanogen value determination which, while giving valuable results, is rather troublesome for use as a routine method in an analyst's laboratory.

The conditions that were chosen as giving a sufficiently selective action while being conveniently attained are embodied in the following definition of the constant (termed subsequently the "oxidation value"):—the amount of oxidation, expressed as g. of iodine per 100 g. of fat, which takes place at 60° C. in one hour, when the fat is dissolved in an excess of a mixture of 10 vols. of a glacial acetic acid solution of crystallised sodium dichromate ($Na_2Cr_2O_7.2H_2O$) of normal oxidising strength, with 2 vols. of carbon tetrachloride.

Previous experiments with different oxidising agents were unsatisfactory. With a mixture of chromic and acetic acids the results were more in line with the iodine value, the total consumption of oxygen being considerably more than when sodium dichromate was used. It was also found difficult to avoid oxidation of the saturated glycerides with chromic acid or potassium permanganate in acid solution, and an acid solution seemed necessary for the development of a volumetric method with sharp end-point.

Although the products of oxidation have not been fully investigated (this not being essential for the purpose to which the results are put) the oxidation value has been calculated on the assumption that 4 oxygen atoms per double bond are taken up; *i.e.* that 1 ml. $N/10 = 0{\cdot}008$ g. of oxygen or 0·003175 g. of iodine.

PROCEDURE.—After one or two variations in the titre of the sodium dichromate the following procedure was adopted.

Solutions required.—(*a*) $N/1$ sodium dichromate: 49·7 g. of pure crystalline sodium dichromate ($Na_2Cr_2O_7.2H_2O$) are dissolved in about 900 ml. of glacial acetic acid (not necessarily of analytical reagent quality) and, after being heated to 80° C. for 5 minutes, the solution is cooled and made up to 1 litre. As thus prepared, the strength is about 0·9 N, which is satisfactory. This solution can be kept in a well-stoppered bottle for as long as the Wijs reagent.

(*b*) $N/2{\cdot}5$ ferrous sulphate: Ferrous sulphate crystals 112 g.; conc. sulphuric acid 30 ml.; syrupy phosphoric acid 100 ml.; in 1 litre. This need not be standardised, but 25 ml. should be slightly stronger than 10 ml. of (*a*).

(*c*) *N*/10 potassium permanganate, recently standardised.

(*d*) Diphenylamine oxidation/reduction indicator: 1 g. in 100 ml. of conc. sulphuric acid.

Method.—Two flasks (150 to 200 ml.) are fitted with loose glass stoppers, then cleaned with sulphuric acid and chromium trioxide, washed and dried thoroughly.

A quantity of the oil or fat, varying according to unsaturation (see Table I), is weighed into one flask and both flasks are placed in the thermostat at 60° C., accurate temperature control being maintained. Two ml. of carbon tetrachloride are pipetted into each, and, after solution is effected, 10 ml. of the sodium dichromate solution are added, the liquids are mixed, and the flasks are stoppered and left at 60° C. for one hour. A little water is then introduced into each flask (this practically stops the reaction) and, with a pipette, 25 ml. of *N*/2·5 ferrous sulphate solution, after which the contents of the flasks are back-titrated with *N*/10 potassium permanganate solution, the same amount of indicator being used for each test. Oxidation value =

$$\frac{\text{ml. of } N/10\ \text{KMnO}_4 \text{ equivalent to oxidising solution used by oil} \times 0{\cdot}3175}{\text{weight of oil taken in g.}}.$$

A rough guide to the amount of oil to be weighed out is given below:

Iodine value	Oil required g.
0 to 30	0·6 to 0·5
30 ,, 60	0·5 ,, 0·3
60 ,, 90	0·3 ,, 0·2
90 ,, 120	0·2 ,, 0·1
120 ,, 180	0·1 ,, 0·05

Results.—The following results were thus obtained:

TABLE I

Oil	Oxidation value		Iodine value (Wijs)	Number of samples
	Average	Range		
Linseed	97·5	94·1–99·4	184	3
Walnut	69·5	—	147	1
Tung	158·8	—	165	1
Soya bean	58·0	—	130	1
Maize	34·9	—	111	1
Cottonseed	41·3	—	105	1
Apricot kernel	21·9	—	105	1
Sesame	39·1	—	104	1
Rape	27·9	27·3–28·5	100	2
Almond	22·0	22·4–21·9	96	3
Arachis	24·4	—	91	1
Castor	51·2	50·0–52·4	85	2
Olive	15·5	14·5–16·2	84	5
Palm	14·6	—	55	1
Cocoa butter	4·1	3·9 – 4·4	37	2
Coconut	1·6	1·6 – 1·6	9	2

TABLE I—*continued*

Oil	Oxidation value Average	Oxidation value Range	Iodine value (Wijs)	Number of samples
Cod liver	94·5	92·7–95·5	164	3
Seal (old)	63·2	—	114	1
Whale (old)	30·2	—	120	1
Sperm	17·8	—	86	1
Lard	12·1	12·0–13·5	65	4
Beef-fat	4·9	4·3 – 5·5	40	4
Mutton-tallow	4·7	4·4 – 5·1	39	4
Butter-fat	7·6	6·0 – 8·9	37	5
Hardened oils, m.p. °C.				
Whale 32/34	4·1	4·8 – 3·4	62	2
,, (D) 34	3·3	—	62	1
,, 40/42	1·9	—	47	1
,, (D) 46	1·6	—	29	1
,, 50/52	1·4	1·6 – 1·3	12	3
Arachis (D) 33	3·2	—	61	1
,, (D) 40/42	3·1	—	56	1
,, ,,	4·5	—	58	1
,, (D) 50/52	1·6	—	37	1
Cottonseed (D) 41	13·1	13·3–13·0	62	2
Coconut	0·6	—	0·6	1

Fats marked (D) were deodorised.

Certain mixtures were made up (involving little change in the iodine value from that of the main ingredient) and from the determined oxidation value the corresponding proportions were calculated (Table II):

TABLE II

Proportions taken	Per Cent.	Oxidation value	Iodine value (Wijs)	Proportions estimated Per Cent.
Lard	60	8·4	64	58
Hardened arachis oil, m.p. 33° C.	40			42
Olive oil	90	18·2	86	89
Cottonseed oil	10			11
Cottonseed oil	80	40·3	106	84
Maize oil	20			16
Cottonseed oil	20	36·0	110	17
Maize oil	80			83
Almond oil	90	22·1	96	96
Arachis oil	10			4
Linseed oil	95	100·2	183	95·6
Tung oil	5			4·4

INTERPRETATION OF RESULTS.—(*a*) It will be observed from these tables that the oxidation values are far from being proportional to the total unsaturation as measured by the iodine values. Fats with similar iodine values may have very different oxidation values; the greater these differences, of course, the more easy becomes the detection of adulteration.

The hydrogenated fats, as a class, seem to give very low results, which make their detection in, say, lard fairly certain. Hydrogenated cottonseed oil proved to be an exception—at least for the two samples examined. Presumably the low figures are partly due to the decrease in the proportions of the more highly unsaturated components as a result of selective hydrogenation.

The position occupied by castor oil in the table is interesting in view of the fact that ricinoleic glycerides are very resistant to atmospheric oxidation.

(*b*) Much work has recently been done on the atmospheric oxidation of animal and vegetable oils, but no data appear to exist with regard to oxidation in a one-phase system, such as we have here. The oxidation value, depending as it does on uncompleted, presumably irreversible reactions, should involve at least as many velocity constants as there are different kinds of unsaturated glyceride molecules to be oxidised. That is, we might expect a measurable difference in the rate of oxidation of oils of widely different glyceride structures. In order to have further evidence on this point the well-known examples of Hilditch's mixed glyceride rule—cacao butter and mutton-tallow—were subjected to a series of tests involving different times, temperatures, and concentrations of acetic acid, carbon tetrachloride and chromic acid without showing any greater difference between them than that slight, constant one due to different degrees of unsaturation.

With atmospheric oxidation, however, the glyceride structure would seem to be involved. Lea[1] gives a series of curves showing the rate of oxidation by molecular oxygen at 100° C., from which, in decreasing order of susceptibility, we have:—cod-liver oil, lard, olive oil, cottonseed oil, beef-fat, butter and castor oil. In decreasing order of oxidation values these stand:—cod-liver, castor oil, cottonseed oil, olive oil, lard, beef-fat and butter-fat.

The position of the double bond in the molecule, which is believed to affect the rate of oxidation,[2] may also influence the results for hydrogenated fats. Hilditch[3] gives the component acids of selectively hydrogenated cottonseed oil as:

	Component acids, per cent.		
Iodine value	Oleic	Linolic	Saturated
72·1	62·0	11·0	27·0
65·2	68·5	3·5	28·0
57·5	67·0	0·0	33·0

from which one of iodine value 62 might contain 68 per cent. of oleic and 2 per cent. of linolic acid. If the "oleic" acid present consisted entirely of the Δ9 : 10 acid, the oxidation value would be [*vide* (*c*), *infra*] 68 × 0·135 + 2 × 0·87 = 10·9 on the fatty acid basis, whereas, the value found was 13·1/0·956 = 13·7. With hardened arachis oil of iodine value 61, if Δ9 : 10 oleic were the only unsaturated acid present, the value would be 72 × 0·135 = 9·7, as against 3·2/0·956 = 3·3 found. Hence, the low results cannot be fully accounted for by the diminution in the content of more highly unsaturated acids. This seems to point to the presence of *iso*-oleic glycerides as a contributory factor.

(*c*) *Relation between oxidation values and component fatty acids.*—If we write oxidation value = *a* × oleic + *b* × linolic + *c* × linolenic fractions of the fat, and consider only those fats having negligible quantities of the very highly unsaturated acids, we can approximately evaluate *a*, *b* and *c*.

Fat	Oxidation value (O)	Sapon. value (S)	$1-\frac{3{\cdot}8S}{16800}$ (V)	Oxidation value on fatty acid basis (O/V)	Per cent. on fatty acid basis		
					Oleic	Linolic	Linolenic
Palm oil ..	14·6	198	0·955	15·3	44	10	—
Lard	12·1	195	0·956	12·7	57	5	—
Olive oil ..	15·5	193	0·956	16·2	81	7	—
Arachis oil ..	24·4	193	0·956	25·5	61	21	—
Sesame oil ..	39·1	191	0·957	40·9	49	38	—
Cottonseed oil	41·3	194	0·956	43·2	30	46	—
Soya-bean oil ..	58·0	193	0·956	60·6	28	54	5
Walnut oil ..	69·5	195	0·956	72·7	18	65	8
Linseed oil ..	97·5	193	0·956	102·0	10	43	38

As the unsaturated fatty acids listed above (mostly as given by Hilditch and his collaborators) are expressed on the total fatty acid basis, the oxidation values were re-calculated on that basis. By substituting these corrected values in the above equation, and solving graphically for those oils having no linolenic acid, we get $a = 0{\cdot}135$ and $b = 0{\cdot}87$ approximately. The value of *c* (1·67) may then be found from the equations for the remaining oils. The average numerical difference between the determined oxidation values and those obtained by calculating back from the component fatty acids and these factors is only 0·8 unit. The less unsaturated fats do not quite come into line with the others:

Fat	Oxidation value on fatty acid basis	Oxidation value calculated from factors and compositions
Mutton-tallow ..	5·0	8·0
Beef-fat	5·1	8·6
Cocoa butter ..	4·3	7·0
Coconut oil ..	1·7	2·7

In the first two on the list the small percentages of palmitoleic acid present have been added to those of the oleic acid.

The sample of maize oil examined also differed—the calculated value being 42·7 and the found 36·5—and it is noteworthy that these differences are all in one direction. Further work is being done on this point.

ORDER OF REACTION.—Determinations of the rate of oxidation of olive oil, under the conditions set forth above, show that the reaction (or rather sum of the reactions) is apparently similar to a unimolecular one. Three different quantities of oil with the same volume of solution were kept at 60° C., and equal volumes were withdrawn from each for titration at definite intervals. "$T\infty$" (∞ equal to 3 days) corresponded with a consumption of 15 ml. of $N/1$ per g., while the times for the completion of any particular fraction of the reaction were approximately the same in all three instances, the time chosen for the "oxidation value" test corresponding with roughly one-third of the completed reaction. Since 1 g. of olive oil should require 26 ml. of $N/1$ for complete rupture, only 60 per cent. of this amount was used. The determination of the order of the reaction was, however, not very satisfactory, as there was no definite evidence of any true end-point being reached.

SUMMARY.—A test has been devised for the detection of adulteration of animal and vegetable fats, which, while giving good and reproducible results, is rapid and suitable for use in routine analyses.

Taken in conjunction with the iodine value, it enables the proportions in a mixture to be calculated with greater accuracy, while for certain purposes, *e.g.* the detection of hardened fats, the test should prove of special value.

The results obtained show the very close relationship (linear) which may be brought about between the component unsaturated fatty acids of a fat and the amount of oxidation in solution.

The number of oils so far tested is admittedly rather limited, but they have all been from reliable sources. Oxidation values of samples received for analysis in the ordinary way have not been included in the list given above, even when the oils were found genuine by the customary tests.

I am indebted to Mr. Tankard, City Analyst, Hull; Mr. Appleyard, The British Creameries, Ltd., Hull; Mr. J. L. Bennet, Messrs. Alder & Mackay, Edinburgh; and Dr. Stokoe, The Craigmillar Creamery Co., Ltd., Edinburgh, for their kind help in procuring samples.

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CHEMICAL LABORATORY
4, LINDSAY PLACE
EDINBURGH

October 1st, 1938

DISCUSSION

Professor T. P. HILDITCH said that he wished in the first place to congratulate Mr. Alexander on the work he had done. It seemed that he had produced a definitely new characteristic for fatty oils or mixtures, which should prove of considerable service. It was, perhaps, remarkable that, with all the attempts that had been made previously, such a simple method of oxidation had not been brought forward before, and the Society was fortunate in having such a method presented to it that evening. He would like to ask Mr. Alexander how far he thought that the ordinary analyst could obtain with ease reproducible results such as had been shown in the paper. It seemed to him, for example, that possibly special attention would be required in thermostatic control, and for the exact maintenance of temperature, time, etc. He would like Mr. Alexander to elaborate in more detail the pros and cons of the oxidation method as compared with the thiocyanogen method, because although the latter was perhaps subject to certain difficulties, he thought that general experience was that, with sufficient attention to detail, it worked quite well; and it seemed to be no more difficult than the method now propounded. With regard to Mr. Alexander's explanation of the varying oxidation values obtained, he thought that glyceride structure would hardly enter into the matter; differences in the nature of the unsaturated acids present were more likely to be the cause. For instance, possible differences in the reactivity to oxidation of *iso*-oleic acids in hydrogenated oils, or of unsaturated acids of varying molecular weight (chain length), as in whale oil, etc., might play a part.

Referring to "inhibitols," Professor Hilditch said that these were not resistant to oxidation. In the case of atmospheric oxidation they could protect a fat, but in this reaction, with a large excess of active oxygen present in the reacting system, they would be almost instantaneously destroyed by oxidation.

Mr. K. A. WILLIAMS offered his congratulations to the author on a very stimulating paper. He thought it a pity that 60° C. had been chosen for the reaction temperature. It was obvious that the temperature must be very closely regulated; and since 60° was not one of the temperatures usually maintained in the laboratory it would mean keeping special apparatus for this test alone if it were adopted as a routine test. He enquired whether it would be possible to use an ordinary incubator temperature or even 100° C. with corresponding alteration to the duration of the reaction. He had noticed with great interest the curious abnormality obtained with hardened oils and wondered if this was in any way due to a protective influence of the minor constituents of the oils concerned. In the case of cottonseed oil in particular he referred to a new waxy constituent of the unsaponifiable matter recently isolated in Mr. Bolton's laboratory, and suggested that this might not be without effect. He very much admired the regularity of Mr. Alexander's formula. He (Mr. Williams) suggested that further valuable information might be obtained by a study of the early stages of the reaction, since it seemed possible that greater differences would occur in the behaviour of different oils at early than at later stages.

Mr. H. E. MONK, referring to the question of temperature, said that the objection was that every author introduced a new temperature which had to be kept constant. The ordinary practising analyst would prefer a lower temperature. Perhaps the author could tell them something about the temperature coefficient. Had he considered the effect of the unsaponifiable matter, especially where this had a high iodine value, or examined the unsaponifiable matter separately by his test?

Mr. ALEXANDER, replying, said that it was of course necessary that the temperature be accurately controlled. It must not change more than plus or minus 0·5°; a constant temperature of 61° C. would make an appreciable difference; the result would be 0·2 unit higher with olive oil. He, personally, had found no difficulty in keeping to this temperature for one hour, even without thermostatic control. He had tested oils at temperatures other than 60° C., but at about that temperature the most selective results were obtained with N sodium dichromate. Using chromic acid, he found that 15° to 20° C. was more satisfactory, although results in general with the latter reagent were more in line with the iodine value. With regard to the rate of oxidation, the systems appeared to behave as though monomolecular reactions were taking place. This was indicated by the empirical constants a, b and c, which were derived, but for olive oil a more complete test, using three different concentrations (0·3 to 1·2 g. of oil per 10 ml. $N/1$), showed that in a definite time a definite fraction of the apparently completed reaction had taken place in all three instances.

He was very interested in Mr. Williams' observations regarding minor constituents; he did not know positively if they had any effect, but considered it unlikely, as the figures under consideration were too great (representing roughly one-third of the total oxidation) to be influenced by traces of unsaturated compounds. The cottonseed oil variation, commented on by Mr. Williams, was shown only by the hardened oil; unhydrogenated oil agreed very well.

The point about unsaponifiable matter was rather similar to that raised by Mr. Williams; he did not see how a quantity present only to the extent of about 1 per cent. at most could affect the results very much. He had not tested the unsaponifiable matter separately.

It had not seemed to him that this wet oxidation was comparable to atmospheric oxidation at all. He thought that the linear relationship found between the component unsaturated acid content and the oxidation values of the different oils showed that this value could not be influenced by the existence of pro- or anti-oxidants.

Mr. Williams had suggested that figures obtained in the initial stages of the reaction might give valuable results. That might be so (*i.e.* "*a*," "*b*" and "*c*" might show even greater differences), but such figures were more difficult to obtain, since the velocity in the early stages was so much higher. The time taken in manipulation was liable to introduce considerable error. Sixty minutes was found to be long enough to give reasonably accurate results in this respect, and yet not be inconveniently long.

In reply to Dr. Hamence, the author said that the figures given for lard showed that the oxidation range was not wide.

Determination of the Essential Oils of White and Brown Mustards

BY R. C. TERRY, M.SC., A.I.C., AND J. W. CORRAN, PH.D., F.I.C.

(*Read at the Meeting, December 7, 1938*)

THE mustard flour of commerce is a mixture of the flours of two seeds: brown or black, mustard (*Brassica nigra*) and white mustard (*Sinapis alba*). Its condimental properties are largely due to the essential principles of these two seeds.

The essential principle, or volatile oil, of brown mustard is allyl *iso*thiocyanate, a fairly stable liquid which lends itself to ready determination owing to its volatility in steam. The essential principles of brown and white mustards are not present as such in the seeds, but are produced from their respective glycosides, sinigrin (potassium myronate) and sinalbin, by the agency of the enzyme myrosin. These reactions, which are known as the resolution of the glycosides, take place when water is added to mustard flour, and consist in hydrolysis of the glycosides according to the following empirical equations:

$$\underset{\text{sinigrin}}{C_{10}H_{16}NS_2KO_9} \xrightarrow{H_2O} \underset{\substack{\text{allyl}\\\text{mustard oil}}}{C_3H_5NCS} + \underset{\text{glucose}}{C_6H_{12}O_6} + KHSO_4$$

$$\underset{\text{sinalbin}}{C_{30}H_{42}N_2S_2O_{15}} \xrightarrow{H_2O} \underset{\substack{p\text{-hydroxybenzyl}\\\text{mustard oil}}}{C_7H_7O.NCS} + C_6H_{12}O_6 + \underset{\substack{\text{sinapin acid}\\\text{sulphate}}}{C_{16}H_{24}NO_5.HSO_4}$$

It would appear in the light of recent evidence that the mechanism of formation of the essential principles is inadequately expressed by the above stoichiometrical equations. This view is supported by the considerable variation in results obtained in ordinary determinations of volatile oil, when made under slightly differing conditions. This is discussed later.

The essential principle of white mustard is of similar condimental importance to that of brown, but there is up to the present no accepted method for its determination. This is due to the fact that it is more complex chemically than the allyl compound, being the *p*-hydroxybenzyl ester of *iso*thiocyanic acid; it is a rather unstable substance, destroyed at a relatively low temperature, and, moreover, not volatile in steam. The method of determination that we have adopted is accordingly an indirect one, based on the resolution reaction shown above. It will be seen from this reaction that each molecule of sinalbin produces one molecule each of hydroxybenzyl mustard oil, glucose and the acid sulphate of an aliphatic base, sinapin.

If, therefore, the sulphate-content of a white mustard flour be determined both before and after resolution by myrosin, the difference will be a measure of the sinalbin (or of the essential principle) contained in the flour. Of these two sulphate determinations made on the flour, the first will be referred to as the "blank" determination, and the second as the determination of the "resolved value."

We have found the determination of this sulphate in the usual manner (*i.e.* with barium chloride) to be an operation of some difficulty. This is due to the presence of interfering substances (such as proteins) in the mustard, and therefore precipitation with benzidine under controlled conditions has been employed in the present method.*

For the determination of the "blank value" it is necessary to destroy the myrosin in order to prevent the resolution reaction; this is done by mixing the mustard with a saturated solution of mercuric chloride, followed by water. Any sulphate naturally present is thus extracted from the flour, and this extract is then treated with benzidine in acid solution, acetone being added to ensure complete precipitation of the benzidine sulphate. The precipitate is filtered off, washed and determined titrimetrically.

For determination of the "resolved value" the mustard is mixed with water and allowed to stand for a time, and the aqueous extract is then treated with benzidine as before. In both determinations a preliminary treatment of the aqueous extract to remove phosphate is necessary.

The following is a description of the method in full. It is applicable to all commercial mustard flour mixtures, as is explained below.

METHOD.—*Reagents.*—The following reagents are required:—(i) ammonia solution: approximately 6 *N* (33 per cent. of ammonia solution of analytical reagent quality); (ii) hydrochloric acid: approximately 2 *N* (20 per cent. solution of hydrochloric acid of analytical reagent quality); (iii) benzidine solution: 4 g. of purest benzidine are dissolved in 200 ml. of water plus 50 ml. of 2 *N* hydrochloric acid and filtered (moulds develop on this solution and it should therefore be filtered occasionally); (iv) acetone: of analytical reagent quality, diluted to 90 per cent., neutral; (v) saturated mercuric chloride solution; (vi) *N*/10 sodium hydroxide solution; (vii) *N*/10 sulphuric acid.

Method.—(*a*) *Determination of the "Resolved Value."*—Four g. of the mustard are weighed into a dry 100-ml. beaker and carefully mixed with 70 ml. of cold water, care being taken to avoid the formation of lumps. The mixture is allowed to stand for 1½ hours at room temperature (16–18° C.) in order to resolve the glycosides, and then filtered cold into a 100-ml. graduated flask, and the residue is washed with sufficient cold water to bring the volume up to about 90 ml.

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* Since this paper was written a method for the determination of white mustard glycosides has been published by K. H. Bauer and A. Holle (*Pharm. Zentralhalle*, 1937, 78, 545). These authors determine the sulphate in mustard extracts, before and after resolution, by means of barium chloride. The solutions are freed from interfering substances by means of potassium ferrocyanide, zinc acetate and acetic acid (Carrez, *Ann. Chim. anal.*, 1909, 14, 187).

One ml. of ammonia solution is added, followed by about 0·2 g. of light magnesium carbonate, and the mixture is made up to the mark and well shaken. It is then left to stand for ½ to 1 hour, during which time a copious precipitate settles; this contains the phosphates. The mixture is filtered through a dry paper, and aliquot portions of 25 ml. are taken for precipitation of the sulphate.

Twenty-five ml. of the filtrate are placed in a 100-ml. beaker, acidified with 1 ml. of 2 *N* hydrochloric acid, treated with 20 ml. of benzidine solution very slowly, a few ml. at a time, with thorough stirring, and left for two minutes to ensure complete precipitation, after which 40 ml. of acetone are added and the liquid is left for 30 minutes.

The precipitate of benzidine sulphate is filtered off on a mat of asbestos, in a glass filter-tube provided with a perforated disc, with the aid of suction and washed well with 25 ml. of acetone; it is then washed together with the asbestos and disc into a flask with 50 ml. of water. Ten ml. of *N*/10 sodium hydroxide solution are added and the whole is heated to boiling and titrated at boiling-point with *N*/10 sulphuric acid, methyl red being used as indicator.

(*b*) *Determination of the Blank Value.*—Four g. of the mustard flour are weighed into a dry 100-ml. beaker, and stirred up with 10 ml. of mercuric chloride solution, added all at once. When all lumps are broken up, 60 ml. of water are added, and the mixture is allowed to stand for 5 minutes. It is then filtered cold into a 100-ml. graduated flask, and the residue is washed with sufficient cold water to bring the volume up to about 90 ml.

Two ml. of ammonia solution are added, followed by about 0·2 g. of light magnesium carbonate, and the mixture is made up to the mark and well shaken. It is left for ½ to 1 hour, for the copious precipitate to settle. The liquid is filtered through a dry paper. Twenty-five-ml. portions of the filtrate are treated with benzidine exactly as in the determination of the "resolved" value, and the precipitate is titrated with *N*/10 sulphuric acid as described.

The amount of sodium hydroxide used in the "blank" titration is deducted from that used in the "resolved" determination. These amounts are, of course, given by the difference between the alkali added and the acid titre in each instance.

Provided that exactly 4 g. of flour are taken in the first place, each ml. of *N*/10 sodium hydroxide solution used is equivalent to 4·8 mg. of sulphate (SO_4) produced in the reaction, and, hence to 0·495 per cent. of allyl mustard oil in a brown flour, or to 0·825 per cent. of sinalbin mustard oil in a white flour.

The glycoside equivalents are:—1·98 per cent. of sinigrin in a brown flour, or 3·67 per cent. of sinalbin (anhydrous) in a white flour, or 4·12 per cent. sinalbin (+5 H_2O) in a white flour.

NOTES ON THE METHOD.—(1) The ammonia and magnesium carbonate are added for the purpose of removing phosphate, which would otherwise interfere with the determination. (2) A fixed small amount of hydrochloric acid is used for re-acidification of the extract before precipitation. Too much produces a precipitate of protein nature, which renders the benzidine filtration very slow.

(3) All the manipulations are carried out in the cold, as some commercial compound mustards contain starch; in this way the starch is removed at the beginning of the determination. If the starch is gelatinised, subsequent filtrations are rendered very difficult. (4) The "blank" value on an ordinary mustard is very low, and will in general be zero. It may thus often be omitted, at the discretion of the analyst. (5) The sulphate is precipitated with benzidine slowly in order to obtain a granular precipitate which can be easily filtered off. (6) It is essential to use acetone of analytical reagent quality, as commercial grades frequently appear to yield a precipitate with mercuric chloride in the "blank" determination. (7) The times and temperatures of resolution must be closely adhered to. Prolonged resolution at high temperatures causes an apparent increase in sulphate, presumably owing to decomposition of essential oils. (8) The entire process must be carried through in a day. On standing overnight the mustard extracts (at any stage in the process) turn green and much of their sulphate is precipitated. Only the benzidine precipitate can be left overnight.

MIXTURES OF BROWN AND WHITE FLOURS.—The method, as detailed, can be used to determine the content of essential oil or glycoside in brown or white mustard alone. However, by combining it with the ordinary volatile oil determination, mixtures of brown and white flours, with or without the admixture of additional materials (such as starch, etc.), can be completely analysed. Such mixtures include the majority of commercial mustard flours. The total sulphate resulting from the resolution of the mixed glycosides is obtained by the present method. The volatile oil distillation method gives that portion of the sulphate due to the brown mustard flour present. The difference is a measure of the essential oil of white mustard.

The method employed for the determination of volatile oil is the usual laboratory method due to Raquet[1] in which mustard is resolved with water and alcohol for 2 hours at 37° C.; the volatile oil is then distilled into dilute ammonia. The distillate is treated with silver nitrate, the sulphide is made to coagulate, and the residual silver is titrated with thiocyanate.

CALCULATION FOR MIXTURES OF BROWN AND WHITE FLOURS.—The following results are typical of those given by an ordinary English brown mustard flour:

Volatile oil, by distillation	1·5 per cent.
Volatile oil, by sulphate method	1·75 ,, ,,

Thus results by the sulphate method are 15 to 20 per cent. higher than those obtained by distillation. This may for the moment be taken as an empirical fact; the matter is further discussed later (p. 171). Hence it is necessary to apply a correction factor of 1·2 in order to make distillation results comparable with those obtained by the sulphate method.

The present method gives a value, S, for the total sulphate (SO_4) evolved by the resolution of the mixed glycosides. If 4 g. of mustard are taken for the determination, each ml. of $N/10$ sodium hydroxide solution $\equiv$ 0·48 per cent. of sulphate produced from resolution of the glycosides.

From an ordinary volatile oil determination, S_b, that part of the total sulphate corresponding with the brown mustard glycoside, is calculated by applying the above-mentioned factor of 1·2:

$$S_b = 0{\cdot}97\ (1{\cdot}2 \times V)$$

where V = volatile oil content.

The sulphate, S_w, due to the white mustard glycoside, is then given by the difference between these two values:

$$S_w = S - S_b,$$

and from this the percentages of essential oils of white and brown mustards in the sample can be obtained by using the appropriate factors:

Essential oil of white mustard = $1{\cdot}72 \times S_w$
Sinalbin ($5H_2O$) = $8{\cdot}59 \times S_w$
Essential oil of brown mustard = Volatile oil result, V
Sinigrin = $4{\cdot}01 \times V$

Typical values obtained for the essential oil contents of English mustard flours are as follows:

Essential oil of brown mustard, distillation method = 1·5 per cent.
,, ,, ,, ,, ,, sulphate ,, = 1·75 ,, ,,
,, ,, ,, white ,, ,, ,, = 3·2 ,, ,,

By using these figures as a basis, the constituents of any mixed mustard flour can be determined with fair accuracy. It must, however, be noted that the essential oil content, even of English flours, is subject to some variation and, therefore, determinations on the original components of the mixture, if possible, will lead to considerably increased accuracy.

Some values obtained by the present method on certain foreign flours are shown below:*

Flour from	Essential oil of white mustard Per Cent.	Essential oil of brown mustard Per Cent.
Dutch yellow seed	2·99	—
Roumanian yellow seed ..	3·08	—
German yellow cake	3·66	—
Montana yellow seed	3·32	—
Montana Oriental seed ..	—	1·36
Cochin seed	—	1·11

Optimum Conditions for the Sulphate Method.—During the investigation of the most favourable conditions for the sulphate determination, the method was examined step by step to ascertain the optimum conditions for each operation.

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* These results were obtained through the courtesy of Dr. M. C. Albrech and Mr. A. Gendreau of the R.T. French Company, Rochester, N.Y., using the present sulphate method.

1. *Reaction of Resolution.*—The following results were obtained:

	Brown flour		White flour	
Temperature at which resolved ..	16° C.	37° C.	16° C.	37° C.
Hours resolved	Essential oil Per Cent.	Essential oil Per Cent.	Essential oil Per Cent.	Essential oil Per Cent.
1	1·69	1·76	3·17	3·27
2	1·74	1·81	3·21	3·31
4	1·77	1·89	3·25	3·39
8	1·75	1·99	3·22	3·54
16	1·81	1·94	3·41	3·82
32	1·88	2·07	3·57	4·06

These results clearly show that prolonged resolution, especially at high temperatures, causes a marked increase in sulphate; this may be due to an oxidation type of decomposition of the essential oil, and is specially noticeable with the unstable oil of white mustard. Resolution at 16° to 18° C. for about 1½ hours, however, produces constant results.

2. *Removal of Phosphate.*—Additions of 0·5 ml. up to 5 ml. of ammonia solution, and of 0·1 g. up to 5 g. of magnesium carbonate to the extract, have no effect on the result.

3. *Acidification of the Phosphate-free Extract.*—Additions of 0·5 to 2 ml. of hydrochloric acid here have little effect; quantities greater than this cause precipitation in the liquid. This precipitate has no effect on the final result, but causes great difficulty in filtration. It is believed to be of protein nature.

4. *Precipitation with Benzidine.*—The following results were obtained with white flour:

Benzidine added, ml.	5	10	20	40	20
Acetone added, ml.	40	40	40	40	0
Essential oil, on 4 g. of mustard flour, per cent.	3·12	3·15	3·22	3·24	3·14
,, ,, ,, 1 g. ,, ,, ,, ,, ,,	—	3·26	3·23	3·27	1·95

These figures show that, to ensure complete precipitation, a considerable excess of benzidine (10 to 30 ml.), together with 40 ml. of acetone, is necessary. The acetone is particularly essential when only small quantities of sulphate are being precipitated, as can be seen from the last column.

PRODUCTION OF SULPHATE FROM GLYCOSIDES.—Eight g. of white mustard flour were resolved for 1½ hours in 100 ml. of water, and divided into two portions. The first portion was resolved in the usual manner, and after removal of phosphate was made up to 100 ml. Portions of 25 ml. were treated with benzidine and titrated as previously described.

The second portion was treated similarly, after having been resolved for a further hour with the addition of 0·100 g. of purest sinalbin ($5H_2O$) dissolved in 10 ml. of water. The following results were obtained:

	Sinalbin ($5H_2O$)	
	I	II
	g.	g.
4 g. of mustard contained	0·5912	0·5925
4 g. of mustard plus 0·100 g. of sinalbin contained	0·6916	0·6919
Difference	0·1004	0·0994

These results therefore establish the theoretical basis of the determination and indicate that the method gives a fairly accurate quantitative assessment of sinalbin and its resolution products.

ANALYSIS OF MUSTARD FLOUR MIXTURES.—The following results were obtained, by various workers, on mustard flour mixtures made up for the purpose:

Mixture	Brown mustard flour Present Per Cent.	Brown mustard flour Found Per Cent.	White mustard flour Present Per Cent.	White mustard flour Found Per Cent.	Cereal addition Present Per Cent.	Cereal addition Found Per Cent.
A	nil	nil	70	69	30	31
B	nil	nil	40	39	60	61
C	32	33	68	65	nil	nil
D	45	47	25	22	30	31
E	48	46	32	32	20	22

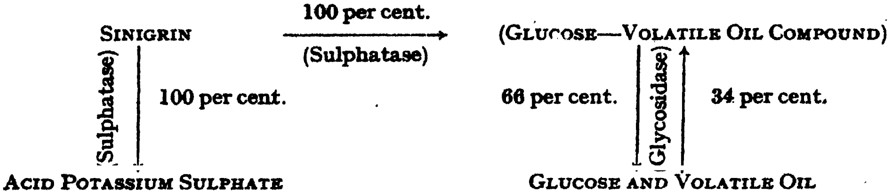
NATURE OF THE REACTION OF RESOLUTION OF MUSTARD GLYCOSIDES.—It has already been noted that when results obtained by the sulphate method and by the volatile oil distillation method are compared, it is necessary to apply a correction factor of 1·2 to the latter in order to make the two comparable. This presumes that the present method gives a true result, and that ordinary volatile oil results are low by about 15 to 20 per cent.

The determination of volatile oil has occupied the attention of a large number of chemists at different times, and consequently a great variety of different methods has been put forward. These chemists have disagreed mainly about the times and temperatures of resolution of the mustard. Thus the original method of Roeser[2] prescribes maceration for 2 hours at room temperature, whilst the official French Codex method gives only one hour at 17° C. In Raquet's[3] modification of the Codex method the maceration is for an hour at 30° to 35°, whereas Carles,[4] and Luce and Doucet[5] recommend only 15 minutes at 40° C. The optimum temperature for liberation of the volatile oil has even been placed as high as 68° to 70° C. by Astruc and Mousseron,[6] though it is known that the enzyme is destroyed at about 80° C.

Additional light has been shed on this problem by the work of Sandberg and Holly,[7] who have examined the resolution reaction of brown mustard under controlled conditions, determining only the sulphate and glucose split off. In the first place they have confirmed the conclusion of von Euler and Erikson,[8] that myrosin consists of two separate entities, a glycosidase and a sulphatase; the sulphatase is responsible for liberating the sulphate group from the glycoside, which is further split by the action of the glycosidase. They further find that only 66 per cent. of the theoretical glucose is split off, whereas the amount of sulphate liberated is as much as 100 per cent. of theory.

If, then, it is assumed that a solution of sinigrin has been resolved by myrosin, 100 per cent. of sulphate has been split off, together with 66 per cent. of glucose. The remaining 34 per cent. of glucose must remain combined with the volatile oil in some intermediate compound; the net effect is thus that only 66 per cent.

of the theoretical volatile oil is produced in this reaction; it is suggested that there may be an equilibrium as follows:



The 100 per cent. reaction takes place by action of sulphatase; the 34 to 66 per cent. equilibrium is catalysed by the glycosidase. Let us then assume that the mixture is distilled. As the temperature rises volatile oil is removed, and the equilibrium changes; the intermediate compound may also be decomposed to some extent. The net result is a yield of volatile oil, varying with conditions.

This hypothesis is put forward as an explanation of the lower results obtained by volatile oil distillation, compared with those given by the sulphate method. Some confirmation is yielded by recent work by Gros and Pichon[9] on the volatile oil estimation. These authors distil off volatile oil *in vacuo* at a temperature not exceeding 70° C.; at this temperature the enzymes are not destroyed. The yields are about 15 per cent. higher than those obtained by the Codex method. If the above explanation is correct, this would enable the equilibrium reaction to go to 100 per cent. completion, owing to the continuous removal of volatile oil.

SUMMARY.—A method has been developed for the determination of the glycosides of white (and brown) mustard. This depends upon determining the sulphate produced from these glycosides by the resolution reaction.

It has been found most expedient to determine this sulphate by precipitation with benzidine, filtration and titration of the precipitated benzidine sulphate.

By the use of this method, in combination with the usual volatile oil method, the essential oils in a mustard flour mixture, such as a table mustard, can be determined and the constituents of the mixture accordingly calculated with a fair degree of accuracy.

Certain discrepancies between the present method and the volatile oil distillation method are noted, and a possible explanation for this is put forward, together with the evidence in its favour.

The authors wish to thank the Directors of Messrs. Reckitt & Colman, Ltd., for permission to publish these results.

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RESEARCH DEPARTMENT
MESSRS. RECKITT & COLMAN, LTD.
CARROW WORKS, NORWICH

September 26th, 1938

DISCUSSION

Dr. H. E. Cox asked why the authors had determined the sulphate when at first sight it would be thought simple to hydrolyse the hydroxybenzyl ester and then determine the hydroxybenzoic acid which would be more specifically characteristic of mustard than was sulphate.

Mr. H. S. REDGROVE remarked that the authors' work had thrown much light on the hydrolysis of sinalbin, and the facts they brought forward certainly seemed to indicate that their theory was correct. One point he wished to criticise was the authors' assertion that the statement that white mustard contained no essential oil was incorrect. What was the definition of "essential oil"? Surely volatility was an essential characteristic.

Dr. CORRAN, replying to Dr. Cox, said that, as analysts, they had aimed at getting the simplest method. Their experience showed that the essential principle of white mustard underwent chemical change very easily on the application of heat. They felt that in such circumstances an attempt to discover a method in the direction indicated by Dr. Cox would have been followed by less success than that claimed for the sulphate method.

Referring to the definition of essential oil, Dr. Corran said that of course there was no essential oil actually in mustard flour. It could hardly be denied, however, that the two pungent oils were regarded as the essential features of mustard. Perhaps the use of the term "essential principles" for these oils and their glycosides might be less controversial.

Electrolytic Determination and Separation of Bismuth

Part I. Determination and Separation in Chloride Solution

BY F. G. KNY-JONES, M.Sc.

(*Read at the Meeting, December* 7, 1938)

THE electrolytic determination of bismuth by deposition from a chloride solution has hitherto presented some difficulty.

Schoch and Brown[1] carried out determinations in solutions containing approximately 5 per cent. of conc. hydrochloric acid with hydroxylamine as depolariser and obtained good results. Engelenburg,[2] however, using similar conditions, found that, while bismuth was deposited quantitatively, the deposit was of a spongy nature and not weighable. Lassieur[3] found that he was unable to obtain deposits suitable for weighing and, after a series of experiments, finally abandoned the problem.[4]

At the beginning of the present work depositions were carried out under conditions similar to those recommended by Schoch and Brown (*loc. cit.*)[1] and the modified conditions previously tried by Lassieur (*op. cit.*).[3] By neither procedure was it possible to control the auxiliary potential at a voltage sufficiently low for the production of a good deposit. After a few minutes' electrolysis the auxiliary potential rose sharply, the deposit became spongy and in some experiments was detached from the cathode. This sharp elevation of the auxiliary potential is possibly connected with the formation of oxychloride in the cathode layer. In order to circumvent this hypothetical cause of trouble, experiments were made to find a substance that would increase the solubility of the oxychloride without at the same time considerably affecting the *p*H. Oxalic acid was tried as a solvent for bismuth oxychloride and found satisfactory.

Depositions were carried out under conditions similar to those employed by the previous workers cited, but with the addition of 5 g. of oxalic acid to 100 ml. of electrolyte. With this modification the auxiliary potential could be satisfactorily controlled and good, adherent deposits were obtained.

EXPERIMENTAL

1. DETERMINATION OF BISMUTH.—The determinations were carried out with the use of the platinum gauze electrodes, saturated calomel auxiliary electrode vessel and voltmeter described by Lindsey and Sand.[5] Measured amounts of bismuth solution were taken. The stock solution was prepared by dissolving pure bismuth in conc. hydrochloric acid (sp.gr. 1·16) containing a small amount of nitric acid and was made up to contain about 10 per cent. of conc. hydrochloric acid.

To the solution taken for each experiment were added a further 10 ml. of conc. hydrochloric acid, 5 g. of oxalic acid, 0·5 g. of hydrazine hydrochloride[6] as depolariser and water to make up 100 ml. The electrolyses were carried out at a temperature of 80–85° C., the current being regulated to give an initial auxiliary potential of 0·15 to 0·17 volt; with higher initial potentials—up to 0·20 volt—deposits tended to be non-adherent. When the current fell to zero or a small residual value the auxiliary potential was raised in the usual manner in steps of about 0·02 volt to a final value of 0·25 to 0·30 volt. Results are given in Table I.

TABLE I

Expt. No.	Bismuth taken g.	Bismuth found g.	Time Minutes
1	0·2501	0·2509	15
2	0·2501	0·2497	20
3	0·2525	0·2525	18
4	0·1010	0·1011	17
5	0·2020	0·2021	22
6	0·2001	0·2002	15

2. USE OF BROWN'S AUXILIARY ELECTRODE.—Some determinations were carried out in which, instead of the glass auxiliary electrode, an electrode of platinum wire covered with bismuth as described by Brown[7] was used. The wire was 0·3 mm. in diameter and was held suspended in the solution by means of a clamp having silver jaws. The clamp was connected with the positive terminal of a 50,000 ohm 1·2 volt voltmeter, the other terminal being connected with the outer electrode. At the beginning of a determination the platinum wire and the outer electrode were placed in parallel by short-circuiting the leads to the voltmeter through a switch. A current of 0·2 amp. was then allowed to flow for 30 seconds, this time sufficing to give the wire a coating of bismuth. The short circuiting

switch was then opened and the P.D. (ΔE) between the wire and the electrode was adjusted to a suitable value by regulating the current.

It was found that a value of ΔE of 0·02 to 0·03V. gave good results; with a higher value the deposit obtained was non-adherent and became detached during the washing process. The wire was weighed with the cathode before and after the deposition. Results obtained are given in Table II.

TABLE II

Expt. No.	Bismuth taken g.	Bismuth found g.	ΔE volt	Initial current in amp.	Time Minutes
7	0·2525	0·2525	0·03	0·4	19
8	0·2313	0·2311	0·02	0·25	27
9	0·1156	0·1156	0·025	0·25	15
10	0·1010	0·1001	0·05	0·4	13

In experiment No. 10 the deposit was non-adherent.

3. SEPARATION OF BISMUTH FROM LEAD AND TIN.—While bismuth may be separated from lead in nitric acid solution, the separation from tin has not hitherto proved satisfactory. Lassieur[8] attempted the separation in nitric acid solution, and also in the same medium with the addition of either hydrofluoric acid or aluminium nitrate. In no instance was there complete deposition of bismuth.

By the use of oxalic acid it has been found possible to deposit bismuth completely in the presence of lead or tin from hydrochloric acid solution. The results in Table III were obtained by using the conditions given in Section 1 and in each determination controlling the auxiliary potential so that its final value did not exceed 0·3 volt. The values in Table IV were obtained by using Brown's auxiliary electrode and following the procedure described in Section 2.

TABLE III

Expt. No.	Bismuth taken g.	Bismuth found g.	Time Minutes	In presence of:
11	0·1000	0·0998	12	0·08 g. of Pb
12	0·1000	0·1004	20	0·10 ,, ,, Sn
13	0·2500	0·2500	29	0·25 ,, Sn
14	0·2891	0·2887	25	0·10 ,, Sn 0·20 ,, Pb
15	0·2891	0·2899	30	0·10 ,, Sn 0·20 ,, Pb

TABLE IV

Expt. No.	Bismuth taken g.	Bismuth found g.	ΔE volt	Time Minutes	In presence of:
16	0·2274	0·2273	0·025	30	0·10 g. of Sn
17	0·1983	0·1983	0·025	30	0·25 ,, ,, Sn
18	0·2004	0·2009	0·02	20	0·10 ,, ,, Pb

4. DETERMINATION OF BISMUTH IN BISMUTH-TIN-LEAD ALLOYS.—Ternary alloys of bismuth, tin and lead are used in the manufacture of sprinkler heads and safety plugs for boilers and for making delicate castings.[9,10]

The application of the electrolytic method to these alloys gives a more rapid method of determining the bismuth constituent than the normal chemical oxychloride separation.[11]

Samples of alloys of known bismuth-content were available through the courtesy of the Chemical Laboratory of Messrs. Siemens Bros. & Co., Ltd.

The determinations, results of which are given in Table V, were carried out as follows:

About 0·4 to 0·45 g. of drillings taken from the alloy were attacked with 1 to 2 ml. of conc. nitric acid. After the reaction had subsided in violence, 10 ml. of conc. hydrochloric acid were added, and the resulting solution was boiled. After the addition of a further 5 ml. of conc. hydrochloric acid, the solution was diluted to 100 ml. with water; 5 g. of oxalic acid and 0·5 g. of hydrazine hydrochloride were then added, and the solution was heated to 80–85° C. The electrolysis was then carried out as described above for the separation from tin and lead.

TABLE V

Alloy	Bismuth in alloy Per Cent.	Wt. of alloy taken g.	Bismuth calc. g.	Bismuth found g.	Time Minutes
A	21·0	0·4005	0·0841	0·0844	18
B	33·3	0·4002	0·1334	0·1332	28
L	51	0·4003	0·2042	0·2046	25
X	49·75	0·4005	0·1993	0·1990	20
L	51	0·4507	0·2299	0·2291	25
B	33·3	0·4523	0·1508	0·1513	35
L	51	0·4245	0·2165	0·2170	26
S	37·6	0·4001	0·1504	0·1507	28

SUMMARY.—By the addition of oxalic acid to the electrolyte it has been found possible to effect a rapid electro-determination of bismuth in chloride solutions under conditions of controlled potential, the auxiliary electrode used being either the saturated calomel electrode of Lindsey and Sand or the wire electrode of Brown.

By means of this method it has been possible to determine bismuth in the presence of lead and tin and hence in ternary alloys of the three metals.

In conclusion I wish to express my thanks to Dr. H. J. S. Sand for his interest and help in this work.

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Nigerian Ginger

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The production of ginger in Nigeria, which was started on a commercial scale about ten years ago as the outcome of the pioneer work carried out by the Department of Agriculture in that colony, has developed rapidly during this period, with the result that Nigerian ginger has won a place among the recognised grades of ginger on the world's market. Large quantities of this ginger were consumed in the United Kingdom up to 1936, and proved quite satisfactory, but certain lots from the 1935 and 1936 crops and the bulk of the consignments of the 1937 harvest, on being submitted to chemical examination, were found not to fulfil the requirements expected for peeled ginger, and in one or two cases legal proceedings followed.

The particulars in which these consignments failed were the percentages of water-soluble extractive and water-soluble ash, for which figures as low as 7·1 and 0·2 per cent. respectively were obtained. The figures used as the criterion of quality are the same as those laid down in the British Pharmacopoeia for peeled Jamaican ginger, *viz.*:

Alcohol-soluble extractive	Not less than 4·5 per cent.
Water-soluble extractive	Not less than 10·0 per cent.
(both expressed on the air-dried material) and	
Total ash	Not more than 6·0 per cent. and
Water-soluble ash	Not less than 1·7 per cent.
(both figures expressed on the material dried at 100° C.).	

On account of this failure to reach the desired standard and the fear of consequent prosecution, the market for Nigerian ginger in the United Kingdom was seriously affected. The lack of demand caused large stocks of this ginger on hand in this country to remain unsold and severely restricted the importing of fresh supplies from Nigeria into the United Kingdom. Although the sale of Nigerian ginger to the Continent was not affected by the lower quality of the product, the difficulty experienced in disposing of supplies in the United Kingdom was of great concern to the authorities and producers in Nigeria. Accordingly, the Department of Agriculture in that colony in collaboration with the Imperial Institute undertook a series of tests to determine the cause of the deficiency in water-soluble constituents of recent crops, that is to say, to ascertain whether it was an inherent feature of the ginger now produced in Nigeria, or whether it was merely due to an unsuitable method of preparation of the ginger.

Various views had previously been put forward to account for this deficiency, but the opinion generally held was that in the preparation of the ginger the rhizomes had been soaked in water for too extended a period, the object of the prolonged immersion being to obtain a pale-coloured product, a pale colour being one of the desiderata of the trade. It was also suggested that the falling off in quality was due to soil exhaustion, but, although this may be true of the ginger produced by a few growers, the natives as a rule move their plantations after two or three years to fresh ground where the crop is often grown on virgin soil. This question, however, is being investigated by the Nigerian Department of Agriculture.

For the purpose of our investigation a large batch of ginger rhizomes was obtained by the Department of Agriculture, Nigeria, and divided into smaller lots, and each lot was treated by one of the six methods (Trials 1, 2, 4, 6, 9, and 11) described in this paper. Samples of the products thus prepared (24 in all) were forwarded to the Imperial Institute, where they were submitted to chemical examination by the British Pharmacopoeia methods. The results obtained are recorded below.

Trial 1.—The rhizomes as harvested, after removal of the roots, were washed free from soil and dried in the sun.

The sample was examined with the following results:

Sample No.	Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
1	6·4	16·3	7·7	5·8

Trial 2.—Dried peeled ginger was prepared from the rhizomes by the method previously advocated by the Department of Agriculture, which yielded a product of a quality hitherto freely accepted by the trade.

The rhizomes were freed from roots and washed free from soil on the same day as they were dug. The next morning they were scraped. While the scraping was in progress the unpeeled rhizomes were stored in water, and as each hand was peeled it was placed in clean water. When scraping was completed the ginger was washed* by gently rubbing and stirring it in six changes of water. As it was necessary to wash the ginger in batches, some of it was soaking* for a considerable time. The average time of soaking between scraping and washing was 1 hour. After being washed the ginger was spread on mat-covered platforms and turned three or four times a day until thoroughly dry.

The dried ginger was soaked for 10 minutes, washed once in water for 5 minutes, then spread out on platforms and dried. This process was repeated eight times, *i.e.* until the required colour was obtained. The products were sampled at the end of each stage of the process, and the samples were examined.

Sample 1 was of light greyish-brown colour and hard. The colour of the hands improved from sample to sample throughout the whole series, No. 10 being very pale buff. As the colour improved, so the ginger became less hard, the hands of Sample 10 being fairly soft.

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[*] "Washing" means stirring and gently rubbing the ginger in water. "Soaking" is used to denote leaving the ginger undisturbed in water.

The samples were examined, with the following results:

Sample No.		Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
1	1st washing ..	6·1	16·6	6·3	5·2
2	2nd ,, ..	5·9	14·8	6·0	4·9
3	3rd ,, ..	5·7	13·7	5·2	4·2
4	4th ,, ..	5·8	13·2	5·3	4·2
5	5th ,, ..	5·6	12·5	5·0	3·9
6	6th ,, ..	5·6	12·5	4·4	3·2
7	7th ,, ..	5·5	12·0	4·4	3·4
9	9th ,, ..	5·4	11·8	4·1	3·2
10	10th ,, ..	5·8	12·0	3·9	3·0

Trial 4.—In order to determine the effect of varying the period of soaking after scraping and prior to the first washing of the hands, separate batches of dried ginger were prepared by the same method as that used in Trial 2, *i.e.* by the Department of Agriculture method, but employing, instead of an initial soaking of 1 hour, a period of 2, 6, 12, 24, or 48 hours.

The five samples were examined, with the following results:

Sample No.		Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
4A	2 hrs. soaking ..	6·0	13·3	3·9	3·0
4B	6 hrs. ,, ..	6·0	12·9	4·3	3·3
4C	12 hrs. ,, ..	6·0	12·6	3·9	3·0
4D	24 hrs. ,, ..	5·9	12·8	4·2	3·2
4E	48 hrs. ,, ..	5·9	12·0	3·8	2·8

Trial 6.—*Native-prepared Ginger.*—In this experiment, the method used to prepare the ginger exported early in 1937 and condemned by the market was followed as closely as possible. The ginger was washed in a basket immersed in a stream, the basket being lifted periodically to allow the water to drain and then re-immersed. After being scraped the ginger was washed for 8 minutes and then dried. It was soaked overnight for 13 hours 40 minutes and washed for 10 minutes; dried; soaked for 6 minutes; washed for 5 minutes; dried; soaked for 5 minutes; washed for 5 minutes; dried; washed for 5 minutes without previous soaking; dried; washed for 5 minutes; dried; washed for 5 minutes; dried. The total number of washings given was thus 7.

The ginger thus prepared was very similar in appearance to Sample 10 of Trial 2, being perhaps slightly better in colour. On examination it gave the following results:

Sample	Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
Native-prepared ..	5·4	8·4	2·4	1·6

Trial 9.—The ginger was prepared as in Trial 2, but the first washing consisted of 3 changes of water instead of 6 changes. The total number of washings was 10.

The resulting ginger was very similar in appearance to Sample 10, Trial 2. It gave the following results:

Sample No.	Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
9	5·2	12·9	4·0	3·3

Trial 11.—The object of this trial was to determine the leaching effect of soaking the dried ginger overnight for 12 hours prior to each of the second and subsequent washings. Seven samples were prepared.

The seven samples were examined with the following results, which are shown in comparison with those obtained for corresponding samples in Trial 2:

Sample No.		Alcohol-soluble extractive Per Cent.	Water-soluble extractive Per Cent.	Total ash Per Cent.	Water-soluble ash Per Cent.
2 (1)	1st washing ..	6·1	16·6	6·3	5·2
11 (1)	2nd ,, ..	5·2	10·2	3·4	2·5
2 (2)	2nd ,, ..	5·9	14·8	6·0	4·9
11 (2)	3rd ,, ..	4·7	7·7	2·3	1·2
2 (3)	3rd ,, ..	5·7	13·7	5·2	4·2
11 (3)	4th ,, ..	4·7	6·9	1·9	0·6
2 (4)	4th ,, ..	5·8	13·2	5·3	4·2
11 (4)	5th ,, ..	4·3	6·5	1·7	0·6
2 (5)	5th ,, ..	5·6	12·5	5·0	3·9
11 (5)	6th ,, ..	4·2	6·5	1·5	0·5
2 (6)	6th ,, ..	5·6	12·5	4·4	3·2
11 (6)	7th ,, ..	4·4	6·0	1·5	0·2
2 (7)	7th ,, ..	5·5	12·0	4·4	3·4
11 (7)	8th ,, ..	4·4	6·2	1·5	0·3
2 (8)	8th ,, ..	(no sample received)			

The following comments may be made on the foregoing results:

Trial 1.—This unpeeled ginger is of satisfactory composition. Its figures meet the standard requirements, with the exception of the amount of total ash; in this connection it may be stated that the British Pharmacopoeia figures are intended to apply to *peeled* and not to *unpeeled* ginger.

Trial 2.—The results show that even after being washed and dried ten times the ginger produced still fulfils the requirements of the British Pharmacopoeia, provided that no prolonged soaking of the dried hands has taken place. It will be noticed that the effect of successive washings is a distinct gradual lowering of the percentages of water-soluble extractive, total ash and water-soluble ash, while the effect on the alcohol-soluble extractive is only slight. The figures also indicate that the ginger does not suffer from any inherent deficiency of water-soluble constituents.

Trial 4.—This experiment shows that soaking the hands for periods up to 24 hours after scraping, and prior to their first washing, has no marked effect on the composition of the ginger. When the duration of the soaking was 48 hours a slight loss of water-soluble constituents took place, but the resulting product was still up to standard.

Trial 6.—The main differences in the methods of preparation of the native-produced ginger of Trial 6 and of Sample 7 of Trial 2 are that the former had prolonged immersion in a stream and a long soaking immediately prior to the second washing. The main differences in the preparation of this native-produced ginger and of Sample 1 of Trial 11 are that the former had a prolonged immersion in a stream and had been washed and dried five times more. Both Sample 7 of Trial 2 and Sample 1 of Trial 11 are up to standard, but the native-prepared ginger of Trial 6 is deficient in water-soluble constituents, and this deficiency would appear to be due to the ginger being kept in water too long.

Trial 9.—The results of this experiment show that reducing the number of changes of water used in the first washing has had the effect of slightly increasing the percentages of water-soluble constituents.

Trial 11.—The results of this trial indicate that soaking the dried ginger for long periods of time reduces very considerably the percentages of water-soluble constituents. The soaking for 12 hours prior to the second washing was sufficient to reduce the percentage of water-soluble extractive by 4·6 below the figure given by the corresponding sample in Trial 2 and the further soaking of 12 hours given prior to the third washing brought the product well below the standard.

The results of the investigation have shown that:

(1) There is no inherent deficiency of water-soluble constituents in Nigerian ginger as represented by the samples examined.

(2) A product of satisfactory quality can be readily prepared, even when the ginger is washed and dried ten times, provided that excessive soaking of the dried, peeled ginger is avoided.

(3) The method of preparation advocated by the Department of Agriculture in Nigeria, which in the past has given a product acceptable to the trade, is satisfactory and can be recommended.

(4) The ginger can be stored in water, after being scraped and prior to being washed for the first time, for a period up to at least 48 hours without serious loss of water-soluble constituents.

(5) The method of preparation as used by the natives in 1937 is unsatisfactory and should not be employed, as the prolonged immersion of the ***dried***, peeled ginger in water reduces considerably the percentage of water-soluble constituents.

(6) Reducing the number of changes of water in the first washing increases slightly the percentage of water-soluble constituents.

(7) Prolonged soaking of peeled ginger, once it has been dried, has a serious adverse effect on the percentage of water-soluble constituents and should therefore be avoided.

With a view to getting the producers to conform more closely to the recommended method of preparation, the Department of Agriculture have adopted a scheme of instruction and educational propaganda. Already, improved results have been obtained, and ginger containing higher percentages of water-soluble constituents has been prepared by the native producers in Nigeria during the past year, but, although the content of water-soluble extractive has been raised to a satisfactory figure, there is still a strong tendency for the water-soluble ash percentage to be below the standard. Nevertheless, it is expected that before long the bulk of the Nigerian ginger prepared will fulfil the requirements of the consumers in the United Kingdom.

SUMMARY.—The present investigation has provided abundant evidence that Nigerian ginger, if properly prepared for the market, conforms to the standards of the British Pharmacopoeia. It shows that the deficiencies in regard to water-soluble constituents, observed in certain samples during 1935–1937, are similar to those produced in these experiments by excessive soaking of the peeled ginger during preparation, and from the information received by the Imperial Institute regarding the manner in which the natives have been preparing the material there is no doubt that the deficiencies referred to are attributable to this cause.

The authors desire to express their thanks to the Director of Agriculture, Nigeria, and the Director of the Imperial Institute, for permission to publish the results of this investigation.

IMPERIAL INSTITUTE
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A Volumetric Method for the Determination of Sulphur and Sulphate Ion

BY BERTIL JOSEPHSON

MANY of the methods proposed for the volumetric determination of sulphur have been tested in this laboratory, but none has proved entirely satisfactory for amounts varying within wide limits. The value of the numerous benzidine methods is restricted by the solubility of benzidine sulphate, which is by no means negligible, and in the acidimetric[1] and alkalimetric[2] methods it is difficult to avoid the influence of either acid or alkaline products of the oxidation. The same source of error is inherent in the methods of titration with lead salt.[3,4] I have found that the most reliable method is to precipitate the sulphate with barium, precipitate the excess of barium with chromate, and titrate the excess of chromate with sodium thiosulphate, as proposed by Andrews.[5]

REAGENTS.—The following reagents are required:

(1) Barium chloride solution: 0·025 molar (6·11 g. per litre).
(2) Hydrochloric acid: 0·2 *N*.
(3) Acetate buffer solution: 530 g. of sodium acetate and 6 g. of acetic acid per litre.

(4) Potassium chromate solution: 0·1622 molar (3·15 g. per litre).

(5) Sodium thiosulphate solution: 0·0075 *N* (11·16 g. per litre); prepared in concentrated stock solution.

(6) Potassium iodate solution: 0·02 *N* (0·7134 g. per litre). This is used as the standard for the thiosulphate solution.

(7) Potassium iodide solution: 10 per cent.

(8) Starch solution: 0·5 per cent. containing a trace of mercuric iodide.

(9) Sulphuric acid: 2 *N*.

(10) Magnesia mixture: 220 g. of magnesium chloride, 110 g. of ammonium chloride per litre.

(11) *N* ammonia solution.

All the chemicals must be of reagent quality and the water used for the solutions should be boiled for 10 minutes.

METHOD.—Pipette into each of three 25-ml. graduated flasks 10 ml. of water or blank oxidation solution (*vide infra*), 2 ml. of 0·2 *N* hydrochloric acid and 2 ml. of the barium chloride solution. These represent the "blanks." Introduce the samples for analysis (not more than 10 ml.) into similar flasks, add 2 ml. of 0·2 *N* hydrochloric acid and 2 ml. of the barium chloride solution (if not already added during oxidation, *vide infra*). After some minutes add 3 ml. of the buffer solution (3) and, after a few more minutes, introduce 5 ml. of chromate solution (4) into each of the flasks, make the contents up to the mark with water and mix thoroughly. After 15 minutes filter through a fine filter-paper (Munktell 00) and pipette exactly 20 ml. of the filtrates into 50-ml. Erlenmeyer flasks. Add 10 ml. of 2 *N* sulphuric acid and 1 ml. of potassium iodide solution (7), leave the flasks in darkness for 15 minutes, and then titrate their contents with sodium thiosulphate solution (5), added from a 30-ml. burette graduated in 0·05 ml., until there is no colour with starch solution (8). The thiosulphate solution should be standardised on the same day against the potassium iodate solution (6).

Modification for Minute Quantities.—A modification for quantities between 0·05 and 0·30 mg. has also been devised. In this modification 5-ml. graduated flasks are used, with one-fifth of the above-mentioned quantity of each reagent, and the titration is carried out with a micro-burette graduated in 0·005 ml. Phosphates, if present, must be precipitated separately, as otherwise they will precipitate the barium. If only very small quantities (less than 0·1 mg.) are present, their influence can be almost completely prevented by the use of magnesia mixture and ammonia, as proposed by Köszegi.[6] Two ml. of magnesia mixture (10) and 1 ml. of *N* ammonia solution are added to the test and blank solutions, and the flasks are allowed to stand for 15 minutes, after which the buffer and chromate solutions are introduced as before. In this procedure the precipitated magnesium ammonium phosphate is dissolved only very slowly by the buffer solution. The effect of larger amounts of phosphates, however, cannot be avoided in this way. Heavy metals, which precipitate the chromate, must also be removed before the analysis. Strong acids and bases, oxidising and reducing substances must also not be present. Hence the method cannot be applied directly to biological liquids, such as urine, unless their reducing power is known. This can be ascertained by making a further blank determination with the same quantity of the sample, which is treated in exactly the same way as in the original test, but without the addition of barium chloride. The titration value thus obtained represents the reducing power and should be subtracted from the value found in the usual way. This method, however, did not give such exact values as were obtained with oxidised samples.

CALCULATION.—The concentrations and amounts of the different solutions have been so chosen that each ml. of the sodium thiosulphate solution in excess of 10 ml. (the volume consumed by the chromate present, *vide infra*) corresponds with 0·1 mg. of sulphur in the original sample. Hence the difference in the titration values for the test and blank solutions corresponds with 0·1 mg. of sulphur for each ml., provided that the concentration of the thiosulphate solution (5) is calculated to that given above.

NOTES ON THE PROCESS.—The solubility of barium sulphate in water, which has been shown by Kohlrausch[7] to be about 1 in 430,000, has no significant influence on the results. Stockholm and Koch[8] found that in very dilute solution precipitation of barium sulphate was incomplete, but their solutions were relatively rich in nitrates, which are known to have a solvent action on barium sulphate. Co-precipitation of barium with the barium sulphate has no influence when the precipitation occurs slowly as in dilute solutions, such as those used in the present method (Treadwell[9]). Moreover, when the precipitate is extracted with hot hydrochloric acid, as in the oxidation process described later, any co-precipitated barium must be redissolved.

In alkaline solution barium tends to form complex chromates or adsorb CrO_3. This is a disadvantage of all methods (Callegari,[10] Norgulis and Hemphill[11]) in which barium chromate is precipitated from an acid solution by an alkaline reagent, such as ammonia or calcium hydroxide. On the other hand, in acid solution barium chromate is soluble, and for this reason Köszegi[6] and Photiadis[12] use sodium acetate as a buffer. The composition of the buffer chosen for this method is that by which the values obtained were most nearly theoretical. The solubility is also diminished by having an excess of $Ba^{''}$ or CrO_4'' ions (Photiadis[12]). In previous methods (*e.g.* that of Klinke[13]), in which the chromate concentration is constant and the barium concentration varies between equivalence with the chromate and lower values, the titration curve will never follow a straight line. It has therefore proved preferable to have a considerable excess of chromate, and this has been arranged to correspond with 10 ml. of the thiosulphate solution in the titration.

Possible sources of error due to the liberation of iodine from the potassium iodide during the titration (Friedrich and Bauer,[14] Manov and Kirk[15]) are negligible with the concentrations and amounts of reagents prescribed in the present method.

OXIDATION OF SULPHUR IN ORGANIC MATERIAL.—As Friedrich and Watzlavek's[1] modification of the Pregl process is tedious, I have adapted the method of E. and M. Kahane[16] to the titration process.

The samples are introduced into small (about 25-ml.) Kjeldahl flasks of Pyrex or Duran glass. Two ml. of the barium chloride solution (1), 1 ml. of pure perchloric acid and 1·5 ml. of pure fuming nitric acid are added, and the flasks are heated gradually to 240° C. in a covered air-bath which is so constructed that the necks of the flasks project outside. After 3 to 5 hours the contents of the flasks will have become a dry white powder (if not, the combustion with 1 ml. of perchloric acid and 1·5 ml. of nitric acid is repeated). The flasks are removed from the bath and allowed to cool; 2 ml. of alcohol saturated with ammonia are introduced, the flasks are replaced in the air-bath, and their contents are evaporated to dryness at 100° C. This treatment is repeated, and the residues are then each extracted with 2 ml. of 0·2 *N* hydrochloric acid on a boiling water-bath for 30 minutes, after which the contents of the flasks are transferred to 25-ml. flasks. The Kjeldahl flasks are rinsed out several times with water, the washings being added to the extracts. The remainder of the procedure is as described above. As in the Pregl method, blank oxidations must also be made, and the resulting solutions used as blanks for the titration.

The wet ashing process is of limited value, since with substances containing phosphorus, heavy metals or volatile sulphur erroneous results are obtained. With the refrigeration method of E. and M. Kahane,[16] also, some volatile sulphur is usually lost. Thus variable results were obtained with cysteine and ichthyol. When the perchloric and nitric acid oxidation was carried out in the absence of barium there was invariably a loss of sulphur trioxide during the evaporation of the perchloric acid.

TABLE I

WET ASHING METHOD

Substance	Concentration	Quantity	Sulphur		
			Calculated Per Cent.	Found Per Cent.	Error Per Cent.
Sulphuric acid ..	0·02008 *N*	0·5 ml.	0·161	0·165	+2·5
				0·163	+1·2
				0·163	+1·2
Sulphuric acid ..	0·02008 *N*	1·0 ml.	0·322	0·319	−1·0
				0·320	−0·6
				0·322	±0
Sulphuric acid ..	0·02008 *N*	4·0 ml.	1·288	1·286	−0·2
				1·288	±0
				1·281	−0·5
Taurine	0·0095 mol.	1·0 ml.	0·307	0·310	+1·0
				0·309	+0·7
				0·313	+2·0
Sodium sulphanilate	0·0114 mol.	1·0 ml.	0·365	0·361	−1·1
				0·369	−0·3
				0·365	±0
Naphthionic acid ..	(14·08 per cent. S)	5·573 mg.	0·784	0·783	−0·1
		3·807 mg.	0·536	0·535	−0·2
		4·384 mg.	0·617	0·616	−0·2
Thiourea	(40·17 per cent. S)	3·000 mg.	1·238	1·276	+3·1
		1·500 mg.	0·619	0·620	+0·2
		1·094 mg.	0·452	0·454	+0·4
		2·189	0·904	0·930	+2·8

Results.—Table I gives a selection of results obtained by the wet ashing method and Table II results by Pregl's method. In the latter method the calculated sulphur-contents were checked by macro analysis, the barium sulphate obtained after oxidation of the substance in a Parr's oxidation bomb being weighed.

Table II

Pregl Ashing Method

Substance	Sulphur-content Per Cent.	Amount mg.	Sulphur		
			Calculated Per Cent.	Found Per Cent.	Error Per Cent.
Crystalline sulphur ..	100	0·861	0·861	0·853	−0·9
		1·145	1·145	1·157	+1·1
		0·436	0·436	0·453	+3·9
Cystine	26·5	2·435	0·645	0·640	−0·8
		2·979	0·789	0·762	−3·4
		2·439	0·646	0·657	+1·7
		2·928	0·776	0·775	−0·1
		1·016	0·269	0·274	+1·9
		0·837	0·222	0·227	+2·3
Taurine	25·60	1·812	0·465	0·467	+0·4
		3·310	0·849	0·854	+0·6
		4·550	1·166	1·157	−0·8
Naphthionic acid ..	14·08	3·979	0·560	0·564	+0·7
		6·577	0·926	0·931	+0·5
		3·968	0·559	0·557	−0·4
Thiourea	41·25	0·987	0·407	0·404	−0·7
		3·052	1·260	1·274	+1·1
		3·329	1·375	1·385	+0·7
Ichthyol	4·83	22·777	1·102	1·114	+1·1
		25·240	1·223	1·138	+1·2

The method has been used in this laboratory for several years with satisfactory results. The sulphur determinations of Ågren and Hammarsten and of Josephson and Jungner were made by the wet ashing procedure and those of Theorell by the dry procedure.

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November 18th, 1938

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A PROPERTY OF RICE BRANS

(*Read at the Meeting of the North of England Section, December* 10, 1938)

THE milling of rice gives either rice bran or parboiled rice bran, according to whether the grain is milled raw or is previously soaked in hot water, treated with steam and dried. Since the prices of the two products differ, and parboiled rice bran is at times appreciably cheaper than rice bran, it is sometimes necessary to decide whether a sample of rice bran contains an admixture of parboiled rice bran.

Rice bran has an average "oil" (petroleum spirit extract) content of about 14·5 per cent., the corresponding figure for parboiled rice bran being about 22·5 per cent.; but the variations are very great, and the amount of "oil" in rice bran may be anything between 10 and 18 per cent., while that in parboiled rice bran may lie anywhere between 16 and 28 per cent.

Microscopic examination of the starch grains is an aid in distinguishing between the two products, and staining reactions help; some evidence can also be obtained from a determination of the percentage of free fatty acids in the "oil"; but these differences are not sufficiently sharp, in our experience, to serve as criteria, and they are of little use for detecting adulteration.

In May, 1936, one of us (F. L. K.) found that when rice bran is sprinkled on the surface of water it floats, unwetted, for a good many hours, whereas parboiled rice bran, or a mixture of the two, begins to sink very soon. The phenomenon is apparently due to differences in wetting properties. Sweat-damaged rice bran also sinks (rice bran has poor keeping qualities, and is liable to suffer from heating and sweating on shipboard or in store); but there is evidence that the sedimentation of parboiled rice bran (liquid cloudy) is different from that of sweated rice bran (liquid clear).

We have obtained and tested rice offals from as many sources as possible (we have had them from every Continent except Australia), and in spite of a number of unproved results (where this "sinking test" indicates the presence of parboiled or of sweated rice bran, and no clear confirmation can be obtained by other tests), we suggest that the method is valuable as affording at least corroborative evidence of admixture or of sweating.

The test can be applied by simply sprinkling the meal on water; but our routine method of applying it is as follows: In the course of the "oil" determination 2 g. of the meal are ground in a mortar with 2 g. of silver sand; when the extraction process is finished, the residue from the Soxhlet thimble is freed from petroleum spirit and poured on to the surface of some water in a beaker; if any appreciable amount of bran sinks within 3 hours, we take it as an indication that the rice bran may contain an admixture of parboiled rice bran, or alternatively, may have been sweat-damaged.

By testing mixtures made up for the purpose we find that addition of 5 parts of parboiled rice bran to 95 parts of rice bran is generally enough to cause sinking within 3 hours. Of the 167 samples of parboiled rice bran examined, all sank in much less than 3 hours.

In tests on 685 samples of rice bran 81 sank in less than 3 hours. Of these 81, we decided that a number were sweat-damaged, while others yielded confirmatory evidence of adulteration with parboiled rice bran; but we know of no satisfactory means of proving our conclusions.

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C. Louden
F. L. Kinsella

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January, 1939

CLASSIFICATION OF RICE BRANS

There has been an attempt, for commercial purposes, to differentiate the two types of rice bran by calling every sample yielding under 16 per cent. of oil, "Rice Bran," and all above that figure, "Parboiled Rice Bran."

To this end a very large number of figures relating to the oil-contents of deliveries extending over 12 months were collected by the Liverpool Seed Oil Cake and General Produce Association, but that arbitrary classification has not been adopted.

I have used the method described in the previous note, and communicated to me by the authors two years ago, and can corroborate their findings.

In addition, I have found that since parboiled rice bran, after the usual grinding and sieving, is bulkier than ordinary rice bran, the weight of a given bulk is a valuable confirmatory test.

If a 10-ml. tube, such as is used for lozenges, is half filled with the sample and tapped on the bench to consolidate the mass, further small portions being added and the tube tapped after each addition until full and it is certain that it can hold no more, the weights of rice brans from various sources vary from 4·44 g. to 5·0 g. (the average being 4·64 g. for 10 ml.), whilst parboiled rice bran seldom varies in weight from 4·02 g. for 10 ml.

A standard Burma rice bran, accepted as such by the trade, when weighed thus by different operators, yielded 4·50 g., 4·56 g. and 4·62 g. per 10 ml.

When mixed with 25 per cent. of parboiled rice bran the weight of 10 ml. was 4·39 g.

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January, 1939

A CONVENIENT METHOD FOR ESTIMATING THE HYDROCYANIC ACID GENERATED BY LINSEED CAKE

(*Read at the Meeting of the North of England Section, December* 10, 1938)

Most linseed cakes, when kept warm and wet, produce prussic acid by the action of an enzyme on a glycoside, and deaths of animals, particularly calves, have at times been attributed to this action. The picrate test for prussic acid has long been known and used, and was studied as a quantitative method by Chapman (Analyst, 1910, **35**, 469), who found that it is not specific for prussic acid and therefore not to be trusted, especially in the analysis of decomposing viscera, where all sorts of volatile compounds might be present, some of which might give the red colour with sodium picrate. Confining our remarks to linseed cake, however, our experience is that:

(1) with many scores of samples, the picrate method has given consistently good results, agreeing with those obtained by other methods;

(2) when carried out as described below, the picrate method is very much more convenient than the usual methods involving distillation with steam; and

(3) the modification of the picrate method suggested here gives important information about the rate of development of prussic acid.

APPARATUS.—About six glass containers are needed, about 3 inches in diameter, and fitted with air-tight lids. Inside each stands a crucible, basin, or flat dish.

REAGENT.—Four g. of picric acid and 40 g. of anhydrous sodium carbonate are dissolved separately in water, mixed and made up to 1 litre.

METHOD.—One g. or 0·5 g. of ground linseed cake (or as much as will give 0·1 to 0·5 mg. of prussic acid) and 10 ml. of water are mixed in a glass container, and 10 ml. of sodium picrate solution are placed in the small basin, which is put into the container. The lid having been put on, the vessel is left in an incubator at blood heat until next day. Standards are made up in similar vessels, a very dilute, slightly acidified solution of potassium cyanide being used in place of linseed cake; these are put into the same incubator. Next morning the picrate solutions are washed into Nessler cylinders and compared.

It is possible to match the test solution with the standards without removing them from the small basins, and even to assess the prussic acid approximately without opening the containing vessels, thus getting some idea of the speed with which the prussic acid is being generated.

RESULTS.—In the Nessler cylinders, differences due to 0·05 mg. of prussic acid (which we consider sufficiently close for our purpose) are very easily seen, and the method will detect 0·005 mg. of prussic acid. We append a table showing some of our results.

Prussic acid produced per 100 g. of meal

Sample No.	Picrate method mg.	Silver nitrate method mg.	Prussian blue method mg.	Iodine method mg.
1	45	45	40	45
2	40	42	40	—
3	60	62	60	—
4	65	65	—	—
5	45	45	43	—
6	45	45	42·5	—
7	42·5	42	40	—
8	42·5	—	42	—
9	80	80	80	—
10	60	60	60	—
11	65	65·6	—	—
12	10	12	—	—
13	75	—	75	—
14	100	—	100	—
15	65	—	65	—
16	35	35·1	—	—
17	40	40	40	—
18	42·5	42·1	—	—
19	40	39	—	—
20	37·5	39	—	—

NOTES.—(1) Permanent standards could, no doubt, be prepared, but we have not found it worth while. We are now getting good results by measuring the colour in a photo-electric colorimeter.

(2) If the standard potassium cyanide solution is pipetted directly into the sodium picrate solution in the small basin, instead of into the outer container, the colours obtained are not quite the same; there appears to be a difference in the quality of the colour.

(3) Good results were obtained even when we allowed decomposition of the linseed cake to take place, rendering other methods of determination difficult or impossible to apply.

(4) Messrs. Towers of Widnes have made a convenient and cheap apparatus for us by grinding the flanges of Pyrex pie-dishes, so that two of them fit together to make a desiccator-like vessel; for the inner basins to hold the picrate solution, they have made flat dishes of glass, with three legs and a central handle.

Rate of Development of Prussic Acid.—We have observed great differences in the speed with which the red colour appears after the apparatus has been put in the incubator; with some of our worst samples (those that produced most prussic acid) the colour reached its maximum in four hours, all the prussic acid having been generated and having reacted with the picrate, while other samples required much longer incubation. The red colour was sometimes visible in 20 minutes, sometimes not for several hours. We suggest that this factor (the rate at which the linseed cake produces prussic acid), which appears to have been ignored hitherto, may be of great importance in any assessment of the toxicity of linseed, particularly with ruminants.

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H. Antrobus

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Liverpool
January, 1939

STANDARDISATION OF HYDROCHLORIC ACID

It has been pointed out by Bjerrum (*Die Theorie der alkalimetrischen und azidimetrischen Titrierungen. Sammlung chemischer und chemischtechnischer Vorträge*, Band XXI, Stuttgart, 1914) that in exact work it is necessary to titrate to some particular hydrogen ion concentration. The object of the few experiments quoted below was to ascertain the difference between the titration value of approximately $N/10$ hydrochloric acid as determined with silver nitrate using adsorption indicators and as determined when titrated to a pH value of 3·8.

The experiments were carried out in a manner similar to those already described with potassium iodide (Analyst, 1939, 64, 112). The same Stas pipette as before was used to deliver 63·73 ml. of hydrochloric acid ($N/10$). The titrations were completed by using $N/100$ hydrochloric acid with tartrazine as the adsorption indicator, and $N/100$ silver nitrate solution with phenosafranine as indicator. The quantity of silver nitrate taken for the titrations in which tartrazine was used was slightly greater than that for quantitative reaction with 63·73 ml. of $N/10$ hydrochloric acid, whereas when phenosafranine was used the weight of silver nitrate taken was slightly less than this amount. The magnitude of the experimental errors in the work was of the same order as in the titration experiments with potassium iodide.

The neutralisation experiments were carried out in a similar manner, but in every instance the quantity of potassium bicarbonate weighed was such as to be slightly in excess of that required for quantitative reaction with 63·73 ml. of $N/10$ acid. The titrations were therefore always completed by running $N/100$ hydrochloric acid into the alkaline liquid. The change of colour with screened methyl orange from the green alkaline colour to the magenta acid colour through the grey tint at which the pH of the solution is 3·8 could be determined to ±0·5 ml. of $N/100$ acid. It was less precise than the colour change with an adsorption indicator. However, the total working error in a determination would probably not exceed one part in one thousand.

1. *Silver nitrate determinations.*

Silver nitrate taken g.	$N/100$ $AgNO_3$ or $N/100$ HCl required* ml.	Indicator	Determined vol. of $N/10$ HCl equiv. to 1 litre of $N/10$ $AgNO_3$ ml.
1·1017	12·5 HCl	Tartrazine	1003
1·0804	1·0 HCl	Tartrazine	1004
1·0164	38·0 $AgNO_3$	Phenosafranine	1002
1·0543	15·5 $AgNO_3$	Phenosafranine	1002

2. *Potassium bicarbonate determinations.*

Potassium bicarbonate taken g.	$N/100$ HCl required* ml.	Indicator	Determined vol. of $N/10$ HCl equiv. to 1 litre of $N/10$ $KHCO_3$ ml.
0·6559	22·0	Screened methyl orange	1005
0·6785	44·5	,, ,, ,,	1005

* After the addition of 63·73 ml. of $N/10$ HCl.

From these experiments it will be seen that there is a small but appreciable difference between the titration values of the acid according to whether the titration is completed with hydrochloric acid using tartrazine or with silver nitrate using phenosafranine as indicator. Taking the average value of 1003 ml. of $N/10$ acid from the adsorption indicator experiments as the most reliable figure, the value of 1005 ml. obtained from the neutralisation experiments in which a final pH of 3·8 was attained is what might be expected. Further experiments on the titration of acids to definite pH values are being carried out. A. J. Berry

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DETERMINATION OF BROMIDE IN PRESENCE OF CHLORIDE

It is not possible to determine bromide in the presence of either chloride or iodide by titration with silver nitrate using an adsorption indicator, because the solubility and adsorptive capacity of silver bromide is intermediate between that of the two other silver halides. The success of the method for titrating iodide in the presence of chloride previously described (Analyst, 1939, **64**, 112) is due to the considerable difference between silver iodide and silver chloride in these respects. Various methods for determining bromide in presence of chloride depending upon differential oxidation have been devised. The oxidising agent must be employed under carefully regulated conditions, as otherwise a certain amount of oxidation of the chloride will take place. One of the best methods of effecting the desired result, originally due to Bugarsky (*Z. anorg. Chem.*, 1895, **10**, p. 387) and modified by Andrews (*J. Amer. Chem. Soc.*, 1907, **29**, p. 275), consists in oxidising the hydrobromic acid to bromine with iodic acid thus:

$$2KIO_3 + 10KBr + 6H_2SO_4 = 6K_2SO_4 + 6H_2O + I_2 + 5Br_2.$$

The bromine and iodine are removed by distillation, and the excess of potassium iodate is determined by adding excess of potassium iodide and titrating the resulting iodine with sodium thiosulphate solution.

In my experiments the oxidation of the bromide was effected in the usual way, but a modification of the procedure was introduced for determining the unused potassium iodate. The solution was reduced by shaking with a 2 per cent. zinc amalgam to convert the iodate into iodide The iodide thus obtained was then titrated directly with a fresh quantity of the original potassium iodate solution. In this way the iodate which had been used in the oxidation of the bromide was determined directly.

It was found that approximately correct results were obtained when the amount of bromide was present in relatively high proportion to the chloride. When, however, the proportion of chloride was considerable, high results were invariably obtained, doubtless owing to oxidation of some of the hydrochloric acid.

The following results were obtained with a standard solution of 3·42 g. of potassium iodate per litre.

(1) A solution consisting of 20 ml. of $N/10$ hydrochloric acid, 20 ml. of potassium bromide solution (11·25 g. of KBr per litre), 50 ml. of standard potassium iodate and about 3 ml. of dilute sulphuric acid was boiled for five minutes and left overnight. The solution was then boiled gently for over two hours, fresh water being added from time to time to replace loss by evaporation. The boiling was continued for some time after the absence of bromine in the steam had been proved by the use of filter-paper impregnated with fluorescein. The residual liquid was then reduced with zinc amalgam and titrated directly with the standard solution of potassium iodate in presence of a high concentration of hydrochloric acid in the usual manner; 13·4 ml. of potassium iodate solution were required.

(2) This experiment was a duplicate of (1). The quantity of standard potassium iodate solution required for the reduced solution was 13·2 ml. If the average titration value of 13·3 ml. is taken, the concentration of potassium bromide is 11·1 g. per litre.

(3) This experiment was carried out to investigate the effect of a high concentration of hydrochloric acid. Twenty ml. of N hydrochloric acid were present, otherwise the same quantities of the other constituents were used, and the boiling was prolonged for nearly three hours. The final quantity of potassium iodate solution required for the reduced solution was 12·2 ml.

(4) This experiment was an exact duplicate of (3). The final volume of potassium iodate solution required was 12·1 ml.

By taking the average titration value of the last two experiments, the concentration of potassium bromide is found to be 12·2 g. per litre.

High results in presence of much chloride have been noted by other investigators (see Sutton's *Volumetric Analysis*, 12th Ed., p. 197). A. J. BERRY

CHEMICAL LABORATORY
UNIVERSITY OF CAMBRIDGE

Official Appointments

THE Minister of Health has approved the following appointments:

HUGH CHILDS as a Public Analyst for the Borough of Chesterfield, in addition to John Evans (December 9th, 1938).

HUGH CHILDS as a Public Analyst for the County Borough of Lincoln, in addition to John Evans (December 9th, 1938).

HUGH CHILDS as a Public Analyst for the County Borough of York, in addition to John Evans (December 14th, 1938).

ALBERT LESTER WILLIAMS as a Public Analyst for the County Borough of Birmingham, in addition to H. H. Bagnall.

The Minister of Agriculture has approved the following appointment since November 25th, 1938:

Eric Voelcker as Agricultural Analyst for the County Borough of Oxford.

H. Childs as Deputy Agricultural Analyst for the County Boroughs of Lincoln and York.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF DEPTFORD

Annual Report for the Year 1937

Of the 505 samples submitted under the Food and Drugs Act, 323 were taken formally.

Pork and Beans.—A prosecution was instituted against the vendors of a brand of canned beans in tomato sauce which was labelled and being sold as "Pork and Beans with delicious Tomato Sauce." The three cans examined contained no pork or pork-fat. Similar preparations have been on sale for many years as "Baked Beans with Pork and Tomato Sauce," and have contained only a very small piece of pork or pork-fat. This latter description might be held to mean simply "Beans with pork- and tomato-flavoured sauce," but the one objected to seems to imply that pork is a major constituent and constitutes a definite departure from the trade practice that has become established. The case was strongly defended, and it was stated that the pork had been introduced, not in its solid state, since customers sometimes objected to finding a piece of "greasy fat" in their beans, but in the form of pork stock, which, being perfectly distributed throughout the sauce, was free from such objections.

The analysis showed none of the normal constituents of pork stock, such as pork-fat, flesh fibres, creatine and other nitrogenous extractives, non-nitrogenous organic and inorganic extractives, which were evident in "control" analyses on samples prepared in the laboratory, and I was therefore able to state that no material quantity of pork stock could have been introduced into the tins which were sampled. This statement was disputed by experts on behalf of the defendants, who claimed that they had proved the presence of pork stock by means of the Gold Number test, and the third portion of the sample was sent to the Government Chemist, whose report confirmed the absence of pork and of any material quantity of pork stock; he was, however, unable to ascertain whether or not a very small proportion of pork stock was present, on account of the decomposition the sample had undergone on keeping since it was bought.

The magistrate took the view that, in any event, pork stock, made from the bones and bellies of pigs should not be described as pork, and, on the defendants indicating that they had already had different labels printed and their real desire for guidance in the matter, dismissed the case under the Probation Act on payment of 25 guineas costs.

H. Amphlett Williams.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

LIABILITY FOR TYPHOID FEVER CONTRACTED FROM MILK

COURT OF APPEAL

Square v. *Model Farm Dairies (Bournemouth), Ltd.*

On January 24th an appeal was heard before Lord Justice Slesser, Lord Justice Clauson and Lord Justice du Parcq, against the judgment of Mr. Justice Lewis, in the second of two consolidated actions in favour of the plaintiffs.

Sir Walter Monkton, K.C., and Mr. Graham Dixon appeared for the appellant company, and Mr. H. J. Wallington, K.C., and Mr. H. Maddocks for the respondents.

The case for the plaintiffs in the original action was that in August, 1936, the defendant company had agreed to supply milk daily for the use of Mr. Square, his family and household. The plaintiffs said that it was a term of the contract, and that the defendants by a letter and a brochure expressly and implicitly warranted that the milk supplied should be clean and free from contamination or infection by disease or otherwise, and should be fit for human consumption. The milk was delivered to the plaintiffs daily from August 1st to 21st, 1936, and the complaint was that the milk, or some of it, was not pure, but was infected with the germs of typhoid fever. Alternatively, the plaintiffs complained that the defendants were negligent in that they had failed to take adequate precautions to ensure that the milk was pure. It was alleged that, in consequence of the defendants' default, Mrs. Square, her two infant children, the governess and Mr. Square's niece contracted typhoid fever and became seriously ill.

The defendants denied negligence or breach of any duty. They did not admit that the letter and brochure sent by them to Mr. Square contained any warranty or representation. Alternatively, they pleaded that, if they made the alleged warranties or representations, these were true, or were made innocently and in the honest belief that they were true. They also denied that they were guilty of any breach of statutory duty.

At the hearing before Mr. Justice Lewis it was conceded that it was from milk sold by the defendants that the infection arose. The Judge ruled that there was no evidence fit to leave to a jury on the charges of fraud, as there was no evidence that the statements in the letter or brochure which had been sent to Mr. and Mrs. Square were untrue, much less untrue to the defendants' knowledge. He also decided that there was no evidence of negligence on the part of the defendants. He held, however, that the defendants were liable in damages to Mr. Square, and also to those of his household who became infected with typhoid fever, by virtue of Section 2 (1) of the Food and Drugs Adulteration Act, 1928, on the ground that that section did not preclude the bringing of a civil action by a person injured through a breach of its provisions, and that the right of action for its breach extended not only to the purchaser but to anyone who suffered damage as a result of it.

It was conceded that Mr. Square was entitled to damages under Section 14 of the Sale of Goods Act, 1893, and these were assessed at £400. The plaintiffs (Mrs. Square, the children, the governess and the niece) in the second action, which had been consolidated with the first action, were awarded sums amounting in all to £525.

The defendants appealed against the award of damages in the second action, and the plaintiffs in the second action appealed against the ruling of the Judge on the question of fraud.

Lord Justice Slesser, giving judgment, said that where there was a statutory duty any person injured through a breach of that duty would normally, in the absence of any remedy in the statute creating the duty, have an action. Where the statute had itself provided penalties different considerations might arise. He proposed therefore to consider the purview of the Act of 1928 in order to see if any remedy was available other than the remedy or penalty specifically provided in the Act itself. In his opinion, the present case was fundamentally different from cases such as *Groves* v. *Lord Wimborne* (14, *The Times L.R.*, p. 493; [1898], 2 Q.B., 402), which dealt with the position where the legislature had imposed a new duty which did not exist at common law. The duties imposed by the Factory and Workshop Act, 1901, were an example, obligations being imposed on employers with regard to those in their employ which in many cases would not in fact arise out of any implied term of the contract between master and servant.

The difference between the case where a new duty had been imposed and the present case was that, in substance, the duty or right contemplated in Section 2 (1) of the Food and Drugs (Adulteration) Act, 1928, was to be found in the provisions of Sections 13 and 14 of the Sale of Goods Act, 1893, which were no more than a consolidation of the existing common law. Although there might be exceptional cases not covered by the Sale of Goods Act, in his opinion Section 2 of the 1928 Act did no more than impose penalties and other consequences in circumstances where there would be a right under the earlier Act to bring a civil action. The protection of the public and the relationship of vendor and purchaser were preserved by the Act of 1928. In other words, that Act was dealing solely with the question of sale of goods as between purchaser and vendor, and was imposing a penalty for doing what might otherwise give rise to a civil action.

It had been argued that, on the facts of the present case, it had not been shown that the defendants had sold an article which was "not of the nature, or not of the substance, or not of the quality demanded." He did not wish to express a concluded opinion on that matter, as the case could be decided on the assumption that the milk sold had in fact not complied with the requirements of the section.

There was yet another reason why the plaintiffs could not succeed in their action under the Act of 1928. It was pointed out in *Monk* v. *Warbey* (51 *The Times L.R.*, p. 79; [1935], 1 K.B., p. 84) that the duty imposed by the statute must be to one whom the legislature wished to protect. He was quite unable to see how it could be said on any view that there was any person to be protected in Section 2 other than the purchaser. The appeal must therefore be allowed.

With regard to the cross-appeals by the plaintiffs against the decision of Mr. Justice Lewis, who held that there was no evidence on the charges of fraud, his Lordship said that, on the interpretation placed by the Court on the letter and brochure sent by the defendants, there was not a shadow of evidence that the defendants did not have a reasonable belief in the truth of what they were saying. The action, so far as based on fraud, had necessarily failed, and the cross-appeals must therefore be dismissed.

Lord Justice Clauson and Lord Justice du Parcq agreed.

Leave to appeal to the House of Lords on the question arising under Section 2 (1) of the Food and Drugs (Adulteration) Act, 1928, was granted.

Imperial Institute

ANNUAL REPORT FOR THE YEAR 1938

In his foreword to the Report the Director, Sir Harry Lindsay, surveys the developments during 1938. The two Advisory Councils and fifteen Consultative Committees (*cf.* Analyst, 1938, **63**, 271) have continued to give the greatest assistance in the work of the Institute. On the Plant and Animal Products side, the two new Committees—on Gums and Resins and on Insecticide Materials of Vegetable Origin—have sketched out the lines of prospective monographs, one on gum arabic and the other on the chief classes of vegetable insecticides. Other monographs in preparation are a treatise on Flax Production and Research in the United Kingdom and a Report on Empire Flax Supplies. On the Mineral Resources side, monographs on Coal, Tin, Magnesium, Bauxite and Aluminium, Chromite and Vanadium are in preparation. A monograph on Manganese was completed and published during the year.

Details of the technical work of the Institute are given in Chapters I and II of the Report. Chapter III describes the Exhibition Galleries, and Chapter IV gives an account of progress made during the year in the Cinema and Empire Film Library and with the lecture programmes.

The investigations to which special reference is made include the following:

Preparation of Tung Oil.—In the course of a study on the preparation of tung oil from the fruits trials were made on the de-husking of *Aleurites montana* fruits by the Chinese fermentation method. The results showed that this method, although suitable for *A. fordii* fruits, did not work satisfactorily with fruits of *A. montana*, which have thick and resistant husks. A better method for *A. montana* consisted in removing by hand the nuts from the fruits, which readily split into segments on drying.

Perilla Seed from Burma.—The sample yielded 44·7 of oil as against the usual 35 to 45 per cent. The oil was of good quality and complied with the requirements of the British and American standard specifications. Perilla seed is not at present marketed in the United Kingdom, but a small amount is occasionally crushed in the United States.

Croton Seed from Nyasaland.—The seed submitted was identified at Kew as *Croton megalobotrys* Muell. Arg. (=*C. gubouga* S. Moore). The seeds contained 37·4 per cent. of shell and 62·6 per cent. of kernel. The kernels yielded 47·3 per cent. of a clear, golden-yellow oil having constants that showed it to be of the "semi-drying" type. The seeds of *C. megalobotrys* have been recorded as showing purgative properties, but it is unlikely that the seeds or oil would find a market for medicinal use.

Ginger from Tanganyika.—A sample of native-produced and untreated material was very moist inside, and was therefore dried and sliced before examination. It then contained 17 per cent. of moisture and yielded 10·8 per cent. of alcohol-soluble, and 17·1 per cent. of water-soluble extractive. The yield of ash, expressed on the moisture-free material, was 5·5 per cent. Brokers in the London market considered that, if properly prepared, the ginger would be comparable in appearance with Sierra Leone ginger.

Mint Oil from Seychelles.—This oil was distilled from specimens identified as *M. arvensis* L. It contained a high percentage of menthol—nearly 82 per cent. as compared with a range of 70 to 90 per cent. in natural Japanese mint oil. The demand for such oil might be limited, as the usual mint oil of commerce is dementholised.

Toxic Roots from Trinidad.—Samples of roots of two plants, employed locally in Trinidad as fish poisons, were submitted in order to ascertain if they were of interest as sources of insecticides. Botanical specimens were also sent and were identified at Kew as *Paullinia leiocarpa* Griseb. and *Serjania paucidentata* DC. Tests showed that the *Paullinia* roots contained no rotenone, saponin or alkaloids, and that the *Serjania* roots were also free from rotenone and alkaloids, but contained a little saponin. It was suggested that the strength of the insecticidal action, if any, might first be ascertained by biological methods and it was proposed to refer the question of the current demand for insecticides in the United Kingdom to the Consultative Committee on Insecticide Materials of Vegetable Origin.

VERMICULITE.—Firms have been requiring Empire supplies of this mineral to replace the American and Russian materials on the market. At present the only known potential sources in the Empire are in the Union of South Africa, Tanganyika and Western Australia. The question of using vermiculite for the same purpose as ground mica in wallpaper printing is under investigation, and samples have been supplied to a firm grinding this class of mica (*cf.* ANALYST, 1938, **63**, 272).

QUARTZ CRYSTALS.—The demand for high-grade quartz crystals both for piezo-electric and optical purposes has become increasingly urgent. The small amount of quartz of good quality received as a result of efforts made by the Institute and others to discover new sources of supply within the Empire has done little towards satisfying the demand for this mineral, which is an essential component of modern devices for telegraphic and telephonic communication.

VANADIUM FROM FUEL-OIL ASH.—Crude petroleum from certain localities, notably South America and Mexico, contains vanadium and, after combustion, the bulk of this remains as oxide in the ash. Since oil-fired boilers are largely used in steamships, it is usual to collect the ash from the furnaces and sell it for its vanadium-content.

SALT FROM BRITISH SOMALILAND.—Two samples of crude salt were sent for analysis and to ascertain if their iodine-contents were adequate for human and animal nutrition. The samples consisted of crude sodium chloride, the chief impurity being calcium sulphate. A trace of iodine was present in one sample, but none was detected in the other. The senders were told that an Institution specialising in nutrition problems had informed the Imperial Institute that, although the provision of a small quantity of iodine is essential to maintain health in man and animals, definite information is not available regarding the minimum amount necessary.

All-India Institute of Hygiene and Public Health

ANNUAL REPORT FOR THE YEAR 1937

THE Report of the Director and Professor of Public Health Administration deals with the activities in the various branches of the Institute during the year (*cf.* ANALYST, 1938, **63**, 116). Among the investigations in progress are the following:

EPIDEMIC DROPSY AND MUSTARD OIL.—Researches of the last three years have indicated that the disease is caused by some deleterious substance introduced through mustard oil, which is almost universally used as a cooking oil in North-Eastern India. Suspicion fell first on allyl *iso*thiocyanate, the pungent principle of the oil, but it was found that the whole of this substance disappeared during the process of cooking. It was also non-poisonous to rats, even when given in large doses. Moreover, the allyl *iso*thiocyanate content of samples of oil obtained from certain families who had been using it for a fortnight or more without ill effects was greater than that of the sample from Jamshedpur, which had given positive results in human experiments. Hence it would appear that the toxic element is probably not allyl *iso*thiocyanate. Since the disease, as thus manifested, is confined to mustard oil consumers only, it is possible that the toxic seeds may be infected with specific moulds or that the toxic substance may be derived from some other seeds or oils which might be added to mustard oil in the course of preparation or sale. Work on these lines is in progress (*cf.* ANALYST, *loc. cit.*)

ASSAY OF FLAVINE AND VITAMIN B_6 IN INDIAN FOODS.—The flavine-contents of about 90, and the (antidermatitic) vitamin B_6 contents of 30 Indian foodstuffs were estimated. Pulses and leafy vegetables were found to be relatively rich, and fruits poor sources of flavine, whilst pulses, cereals and fish gave the best results for vitamin B_6.

EXCRETION OF VITAMIN B_1 IN HUMAN URINE.—The daily excretion of vitamin B_1 was studied in five normal healthy subjects fed on different diets. It varied between 6·4 and 12 per cent. and, having regard to the previous dietetic history of the subjects, it varied in general in proportion to the amount ingested. There was, however, some evidence to show that the excretion of B_1 (total caloric and B_1 intake being kept constant) was much lower in those taking a carbohydrate diet than in those on a diet rich in fat. This would suggest the possibility that the metabolism of carbohydrates demands a greater amount of vitamin B_1 than that of fats.

RÔLE OF ASCORBIC ACID IN MALARIA.—It has been found that during the malarial paroxysm the body excretes vitamin C in considerable amounts, and that as a result of repeated attacks of malaria a condition of sub-clinical hypovitaminosis develops. In view of the important relationship between vitamin C and the reticulo-endothelial system, it is possible that the results of this investigation may throw some light on the rôle of vitamin C in the cure of malaria and in prevention of relapses.

BIOCHEMICAL CHANGES IN THE BLOOD IN ANAEMIAS.—The investigation of the two types of haemoglobin in connection with anaemias has been continued, and systematic estimations of glutathione have also been made. The evidence so far obtained indicates that the percentage of alkali-resistant haemoglobin varies between 8 and 17 per cent. in normal subjects, and that little or no variation occurs in the anaemia of either hyperchromic or hypochromic type. In this respect these anaemias differ from pernicious anaemia, in which reduction and disappearance of the alkali-resistant type has been recorded. The glutathione-content of the blood appeared to vary with the percentage of haemoglobin.

Bengal

ANNUAL REPORT OF THE CHEMICAL EXAMINER'S DEPARTMENT FOR THE YEAR 1936

WITH the creation of the separate province of Orissa the medico-legal and other analytical work of the province is being carried out in the same way and on the same terms as were in force for the combined province of Bihar and Orissa. The Department is controlled by Dr. K. N. Bagchi.

During the year under review 7747 articles were examined as compared with 7422 in the previous year. In the medico-legal section 5784 articles connected with 2347 cases were examined as compared with 6158 articles in connection with 2470 cases in the previous year.

The following were some of the important investigations that were carried out:

COCAINE.—Of 459 samples examined, only 29 consisted of pure cocaine hydrochloride, the remainder being novocaine or cocaine adulterated with novocaine, aspirin, soda, lime, etc.

OPIUM.—Only 38 of the 160 samples examined were genuine in accordance with the Excise Act.

ARROW POISON FROM ASSAM.— A sample of a dark gummy substance used by the hill tribes of the Naga Hills, Assam, for poisoning arrow-heads was submitted by the Deputy Commissioner, Naga Hills. A preliminary investigation was made with the help of the Pharmacological Department of the Tropical School of Medicine, Calcutta. To some extent the action of the poison is similar to that of *Antiaris toxicaria*, but it is ten times more toxic to cats. Its most peculiar characteristic is that it has no ill effect upon toads. Further work on the identification of the poison and the discovery, if possible, of a suitable antidote is in progress.

HUMAN POISONING CASES.—Of the 878 human viscera examined, 40 were received in connection with abortion cases. Poison was detected in 336 specimens, *i.e.* 38·2 per cent. as compared with 27·9 per cent. in 1935 and 25·8 per cent. in 1934. As usual, the poison most frequently detected in human poisoning cases (*i.e.* in viscera, vomit and excreta) was opium. It was detected in 171 specimens—35·4 per cent. of the detected poisons. Alcohol, arsenic, atropine, aconite, oleander and hydrocyanic acid came next in the order given.

ANIMAL POISONING CASES.—Poison was detected in 58 of the viscera of 94 horned cattle received. Arsenic was found in 52, oleander in 3, strychnine and brucine in 1, aconite in 1, and a cyanogenetic compound in 1. Thirty-two articles suspected to be cattle poisons were received. In 21 poison was detected—white arsenic in 13, arsenic sulphide in 3, cyanogenetic compounds in 3, copper sulphate in 1, and oleander in 1.

BAHERA (*TERMINALIA BELLERICA*) POISONING.—A Hindu male child, about 4 years old, swallowed some bahera fruit about 24 hours before his death, and was brought to the hospital in a comatose condition. At the post-mortem examination the stomach was found to be healthy. Both sides of the heart contained blood. The membranes were congested and there was a slight meningeal haemorrhage. No poisonous substance could be detected in the viscera, and attempts to isolate a toxic principle from extracts of the fruit (pericarp and kernels) were unsuccessful. Similar cases, in all of which the victims were little children who developed symptoms almost identical with those described, were reported elsewhere. Further investigation to discover the poisonous principle is urgently required.

AKANDA (MADAR JUICE) POISONING.—A boy of about 8 was given some *Akanda* juice (*Calotropis gigantea*) with milk for "treatment of dog bite." Immediately afterwards he became restless and there was vomiting and purging, followed by convulsions and death in about half-an-hour. Madar juice was detected in the vomit, in a piece of cloth with brownish stains said to be faecal stains, and in the viscera (*cf.* ANALYST, 1930, **55**, 683; 1931, **56**, 665; 1932, **57**, 717; 1934, **59**, 37, 542; 1935, **60**, 759). The stomach wall was found congested and oedematous.

SUSPECTED *BONDUCELLA* POISONING.—The viscera of two women said to have died about 3 hours after taking the pulp of *nata* seeds (*Bonducella caesalpina*) were received. The pulp of *nata* seeds is usually taken as a cure for fever and is not known to have been used for criminal purposes. In post-mortem examination the organs did not show characteristic features of poisoning except a congested patch of mucous membrane in one of the stomachs. No poisonous substance could be detected in the viscera.

About 1 lb. of *nata* seeds were obtained and analysed. The glycoside bonducin (*J. Indian Acad. Science, U.P.*, 1934, Vol. **4**, Part 2) was isolated and administered to experimental animals, but produced no ill effects. The extracts of the pulp with various solvents were also non-poisonous. The actual cause of the death of the two women remained unexplained.

NITRIC ACID POISONING WITHOUT CHARACTERISTIC STAINING.—The viscera of a man who died from swallowing nitric acid were examined. There was a black mark extending from the lower lip to the chin, and nitric acid was detected in the stomach and in the empty bottle found by the man's side. The post-mortem examination showed ulceration and a large perforation (2 in. by 2½ in.) in the posterior wall of the stomach. There were also patches of blackening of the mucous membrane of the stomach, but there was no yellow staining anywhere. No trace of sulphuric or acid other than nitric was detected.

ACONITE IN COUNTRY LIQUOR.—The viscera of a Hindu, about 20 years of age, were submitted. He and two other men had drunk *pachai* sold by an unlicensed vendor. All felt sick and had pains in the head and a burning sensation in the stomach. There was vomiting and all became unconscious in about 3½ hours. One died next morning and the others recovered. Aconite was detected in the viscera and in the sample of *pachai*. Sometimes aconite along with datura seeds or *kuchila* (nux-vomica) is mixed with *bakhar*—the fermenting agent containing crude yeasts—with the idea of increasing the intoxicating properties of the liquor. In these cases poisoning is usually accidental.

CHOPPED HAIR AND NAILS AS POISON.—A tuft of chopped hair and small fragments of human nails, together with a vegetable root, were detected in the vomit of a Muhammadan. They had been given with rice and vegetables by his wife. No poison was detected in the root. Chopped hair is frequently used by cattle poisoners, but it is the first time that it is known to have been given to a man. The object of giving these substances is unknown, but they were probably intended as love-philtres. The woman was prosecuted under Sec. 328, I.P.C. (Poisoning).

Home Office

HYDROGEN CYANIDE (FUMIGATION)

STATUTORY RULES AND ORDERS, 1938. NO. 1578*

THESE Rules, which came into force on February 1st, prescribe that notice of any forthcoming fumigation shall be given to the officer in charge of the nearest police station and to the Medical Officer of Health not less than 48 hours before the fumigation. No fumigation shall be carried out except by an adequate fumigating staff, and effective means shall be taken to ensure that persons other than the staff are not present and to prevent contamination of liquids and foods. After the fumigation tests shall be applied to ensure that the area is free from danger, and any adjoining buildings shall be kept under observation to discover any penetration of the fumigant and to safeguard the occupants of such buildings. All bedding, clothing, etc. which have been exposed to the fumigant shall be treated as prescribed, and tests shall be applied to ascertain that they are free from danger. The particulars relating to each fumigation shall be entered in a register which shall be kept by the person who undertakes the carrying out of the fumigation.

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* THE HYDROGEN CYANIDE (FUMIGATION OF BUILDINGS) REGULATIONS, 1938, DATED DECEMBER 19, 1938, MADE BY THE SECRETARY OF STATE UNDER SECTION 1 OF THE HYDROGEN CYANIDE (FUMIGATION) ACT, 1937 (1 EDW. 8 & 1 GEO. 6, c. 45). 1939. H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 2d. net.

Dominion of South Africa

ANNUAL REPORT OF THE DIVISION OF CHEMICAL SERVICES FOR THE YEAR 1938

THE Division of Chemical Services is a branch of the Department of Agriculture and Forestry, but also supplies chemical services to other State Departments that require them, notably to the Departments of Public Health, Justice, Customs and Excise, Lands, Defence and Interior. It is under the direction of Dr. J. P. van Zyl.

ARSENIC ON FRUIT.—One of the regulations under the Fruit Export Act (No. 17 of 1914) is that "no fruit showing visible spray stains or fruit which may contain more than 1/100th grain per pound of arsenious oxide shall be allowed to be exported." Of the total samples examined at Capetown and Port Elizabeth during the season January to April, 1938, 204 contained arsenic in excess of 1/100 grain per lb. However, only 5 samples gave results exceeding the 1/50 grain per lb. permissible under the regulations of the Food, Drugs and Disinfectants Act of South Africa. Some growers have difficulties in complying with the regulations, but certain larger growers who have introduced scientific washing machines experience no difficulty. This may in some measure account for the fact that the percentage of samples exceeding the 1/100 grain limit was only 4·6 at Capetown as against 7·2 at Port Elizabeth.

PUBLIC HEALTH.—Of the 4476 samples examined under the Food, Drugs and Disinfectants Act, 509 were adulterated or below standard. Of this total, 3129 were milks, of which 292 were adulterated or below standard. These figures are much the same as for the previous year and reflect a somewhat high percentage of adulteration.

Ice-Cream.—According to the regulations ice-creams must contain at least 10 per cent. of milk-fat. Of the 215 samples examined, 56 (26 per cent.) were adulterated. Although most of the large and reputable firms supply ice-creams containing more than the required percentage of milk-fat, there must be a number of dealers producing ice-creams of inferior value.

FLUORINE IN CITRUS FRUITS.—Experiments to ascertain the extent to which fluorine is absorbed by citrus fruits are being continued, and the fluorine-content of oranges sent to the London market from various parts of the world is being determined. The results so far obtained indicate that traces of fluorine are frequently present.

TRIORTHOCRESYL PHOSPHATE IN SOYA-BEAN OIL.—In the early part of the year a so-called "mystery disease" occurred in Durban and an investigation was carried out in the Johannesburg laboratory. The Government Pathologist at Durban formed the opinion that the problem was probably a chemical one and invoked the assistance of the division to investigate the possibility of a consignment of soya-bean oil having been the cause of the alleged disease. After an investigation lasting some months it was established that the oil contained triorthocresyl phosphate, a substance which some years ago had produced an epidemic of a similar nature in U.S.A. (*cf.* ANALYST, 1938, **63**, 813).

ABSORPTION OF FLUORINE BY CROPS.—The uptake of fluorine by various crops and grasses is being studied by pot culture. The different materials used comprise not only those rich in fluorine, but also commercial phosphatic fertilisers such as rock phosphate, which sometimes contains as much as 3 per cent. of fluorine, and superphosphate. Judging by appearance alone, the plants receiving a high dressing of sodium fluosilicate show very marked symptoms of poisoning. Analyses to show the amounts of fluorine taken up by the plants themselves are in progress.

"SOOTY BLOTCH" ON CITRUS AND ORANGE.—Until recently a mixture of chloride of lime and boric acid has been used to remove "sooty blotch" from oranges, but it has been found to lose its bleaching properties rapidly. For citrus better results were obtained by the use of a mixture of sodium carbonate, chloride of lime and boric acid. The fruit is readily bleached and keeps well subsequently, but it is essential to coat metallic parts of the containers with a suitable paint or enamel. For the removal of "sooty mould" from oranges a mixture of sodium metasilicate and borax was found to be the most suitable.

Effect of Moisture on the Intake of Phosphorus and Nitrogen.—In the cultural experiments in pots the findings of the previous year were confirmed. Under dry-land conditions phosphate response alone is noted, whilst under irrigation or heavy rainfall response to nitrogen as well as phosphate is shown. The depressing effect of large quantities of potash on the grain yield were again noted.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Effect of Exterior Temperature on Cooking Losses of Meat. A. M. Child. (*J. Agric. Res.*, 1938, **57**, 865–871.)—The cooking losses of (1) semitendinosus beef muscle, of (2) longissimus dorsi beef muscle, heated to 58° C. internally, and of (3) longissimus dorsi pork muscle heated to an internal temperature of 84° C. by roasting at various oven temperatures were studied. With (1), twelve samples were cooked at each of the following temperatures:—125°, 150°, 175° and 200° C. The cooking losses increased with the exterior oven temperature owing to losses from evaporation. Standing beef ribs (2) cooked at constant oven temperatures of 150° and 200° C. and at 150° C. following searing at 260° C., showed greater losses at the two latter temperatures than at 150° C. constant temperature, the loss at 200° C. being the greatest. With pork loin (3) cooked at 125°, 150° and 175°, and at 150° C. after searing for 20 minutes at 260° C. the cooking losses were not affected by oven temperature. Thus cooking losses are increased with the exterior temperature for meat cooked to 58° C. internally, but not in meat cooked at 84° C. internally. The press-fluid from the roasted meat is not affected by exterior oven temperatures, and the force required to shear the meat is only affected at 125° C. and lower (low shear force), and at 200° C. and higher (high shear force). The Warner–Bratzler apparatus, which was used for the shear test, is described. E. B. D.

Detection of Sucrose, Hydrogen Peroxide, Formaldehyde and Nitrates in Milk by means of Sulphuric Acid. E. Bohm. (*Z. Unters. Lebensm.*, 1939, **77**, 18–32.)—The adulteration of milk with sugar is limited to about 1 per cent. owing to the fact that concentrations approaching 2 per cent. are detected by taste. When 9 parts of milk are mixed with 1 part of a 10 per cent. sucrose solution the figures for the density, refraction (calcium chloride serum) and depression of freezing-point are slightly greater than the corresponding figures for the original milk. The majority of methods for the detection of sucrose in milk depend upon the preliminary preparation of a serum, but the method to be described is free from this disadvantage, a definite amount of conc. sulphuric acid being added directly to the milk. The milk (2 ml.) is mixed either with 2 ml. or with 4 ml. of concentrated sulphuric acid and shaken until all curd is broken up, and the colour of the mixture is observed after 10 minutes. With milk containing no sugar the 2 : 2 mixture shows no change in colour, but in the 2 : 4 mixture a faint rose colour is developed. With milk containing 0·1 to 0·5 per cent. of sucrose the 2 : 2 mixture is coloured a light to deep rose and the 2 : 4 mixture a deep raspberry or red. Limitation of the time of reaction to 10 minutes precludes participation of lactose in the reaction. The temperature of the mixture should not rise above 50° C. and, since the reaction does not take place even with 0·5 per cent. of sucrose at 15°.C., unnecessary cooling must also be avoided. Examination of the course of the reaction shows that the colour is produced by condensation of hydroxymethylfurfural derived from fructose with tryptophane derived from casein and albumin. It is prevented by the presence of 0·4 per cent. of hydrogen peroxide, a yellow colour being formed. With lower concentrations (0·4 to 0·2 per cent.) of hydrogen peroxide the colours are modified to beige, brown and reddish-violet and with concentrations less than 0·02 per cent. the colours due to sucrose are merely weakened. The test may therefore be used to detect the presence of hydrogen peroxide. In the absence of formaldehyde and nitrates any deviation from white in the 2 : 2 mixture and red in the 2 : 4 mixture to brown or yellowish-brown indicates the presence of hydrogen peroxide. The presence of formaldehyde also interferes with the test. With the 2 : 2 mixture a deep yellow colour is formed. With a formaldehyde concentration of under 0·004 per cent. a rose-red colour is formed in the 2 : 2 mixture and a pale violet colour in the 2 : 4 mixture. Very low concentrations of formaldehyde may simulate small amounts of sucrose. If in both mixtures no deviation from the colour reactions of unadulterated milk occurs, the milk may be assumed to be free from formaldehyde. Amounts of nitrate up to 11 mg. of nitric anhydride per litre, such as may occur in watered milk, do not interfere with the test for sucrose, but amounts of 50 mg. or more per litre, which are not to be expected in milk, prevent the reaction even when the sucrose concentration is 0·5 per cent. By the following procedure the test is adapted to the detection of nitrates:—The milk (2 ml.) is mixed with 0·1 ml. of 0·8 per cent. formaldehyde solution (1 ml. of commercial 35 per cent. formalin diluted with water to 450 to 500 ml.), and sulphuric acid is added in the ratio 2 : 4. In the presence of nitrates a blue-violet colour is formed and 3 mg. per litre of nitric anhydride are thus detectable. The applicability of these tests to cream has not yet been investigated. A. O. J.

Presence of Glycerol in Juice of Ripe Olives. H. Marcelet. (*Compt. rend.*, 1938, **207**, 869–870.)—The oil obtained by expression from the ripe fruit is accompanied by an aqueous brown juice. In one test this was found to contain 0·19 g. of free glycerol and 0·47 g. of combined glycerol per litre together with small amounts of various hexoses. S. G. C.

Pectin from Various Sources. Determination of the Strength of Gels. L. H. Lampitt and R. W. Money. (*J. Soc. Chem. Ind.*, 1939, **58**, 29–32.)—The pectin from various fruits, ripe or unripe, is prepared by submitting the chopped or pulped fruit directly to autoclaving and filtration, and the juice or extract is partly purified by three precipitations from water with 70 per cent. alcohol. The precipitated pectin is separated, washed with acetone and finally air-dried, and a 5 per cent. solution in water of the powder used. If the "leaching" method is used in the preparation, a great deal of the pectin of ripe fruits is lost. Neither method produces an ash-free pectin, for which recourse must be had to dialysis. The alcohol precipitation is fairly effective in removing organic impurities, *i.e.* acids and sugars. The gel strength was measured by the torsion apparatus previously described (*J. Soc. Chem. Ind.*, 1936, **55**, 88T). There is a very great difference in strength of gel given by the various pectins; *e.g.* to give a strength equal to 100 angular degrees the equivalent concentrations of pectins were: apple, 100; gooseberry, 158; raspberry, 300; plum, 364; blackcurrant, 400. The linear relationship of strength to pectin concentration (*J. Soc. Chem. Ind.*, 1937, **56**, 290T) previously recorded for gelatin and for pectin was observed in every instance, but considerable variations in the slopes of the lines were noted, perhaps owing to the presence of compounds estimated as calcium pectate, but possessing differing powers of gel formation. Although for apple pectin the slope is independent of the *p*H value and of the sugar concentration, with raspberry, plum, and particularly blackcurrant, the slope is apparently dependent on the *p*H value. With apple pectin the gel strength increases to a maximum as acidity is increased, but with other pectins a continuous increase in strength with increasing acidity is observed over the range employed. When the sugar concentration in the gels varied from 55 to 80 per cent. with apple pectin the curve appeared to tend towards a maximum, owing to increased rate of setting, whereas with the other pectins no such tendency was found. It is to be expected that the compounds associated with the true pectin will vary owing to different degrees of ripeness of the fruit, and such compounds may also be the cause of anomalies in the experiments on effects of acidity and sugar concentrations, and differences in rate of setting of the pectins.

D. G. H.

Iodimetric Determination of Small Quantities of Glucose. E. C. Noyons. (*Rec. Trav. Chim. Pays-Bas.*, 1939, **58**, 17–22.)—The iodimetric method (*cf.* Kolthoff, Abst., ANALYST, 1923, **48**, 386; Hinton and Macara, ANALYST, 1924, **49**, 2) has been adapted to the determination of small amounts (0·2 to 2 mg.) of glucose. A definite quantity of the glucose solution (in the test experiments this was prepared by recrystallising glucose from absolute alcohol, drying it to constant weight and dissolving it in 500 ml. of twice-distilled water) is made up to 10 ml. with twice-distilled water in a 100-ml. stoppered Erlenmeyer flask, mixed with 1 ml. of *N*/10 iodine solution, and treated with 1 ml. of *N*/5 sodium hydroxide solution. The closed flask is allowed to stand at room temperature for 30 minutes, after which 6 ml. of 25 per cent. hydrochloric acid are introduced, and the excess of iodine is titrated with *N*/200 sodium thiosulphate solution. Increasing the alkalinity of the solution gives low results, and increasing the temperature gives high ones. To ascertain the effect of substances likely to have a disturbing effect determinations were made in presence of such quantities of acetone, urea, uric acid, lactose, hippuric acid, creatine, creatinine, galactose, alcohol, glycerol and lactic acid as occur in blood, and the results (which are tabulated for creatinine, alcohol, glycerol, lactic acid, acetone, urea, uric acid, and hippuric acid) led the author to test the method for the determination of glucose in blood. The method of Fujita and Iwatake, who used precipitated cadmium hydroxide to de-albuminise the blood (*Biochem. Z.*, 1931, **242**, 48), was investigated, but was unsatisfactory in unbuffered solutions. The use of a buffer solution containing 50 ml. of *M*/potassium dihydrogen phosphate solution mixed with 75 ml. of *M*/sodium hydroxide solution was investigated, both with and without the de-albuminising agent. In absence of the de-albuminising agent the procedure was as described above, except that 1 ml. of the buffer solution was used instead of the sodium hydroxide solution and the time of oxidation was increased to 40 minutes; the results were more satisfactory than with sodium hydroxide solution. In presence of the de-albuminising agent, the method was as follows:—Two ml. of glucose solution were added to 16 ml. of a solution containing 13 g. of cadmium sulphate and 63·5 ml. of *N* sulphuric acid per litre, and 2 ml. of 1·1 *N* sodium hydroxide solution were added. The mixture was shaken for some time and then centrifuged. To 5 ml. of the centrifugate were added 1 ml. of *N*/10 iodine solution, 1 ml. of buffer solution, and 5 ml. of twice-distilled water, and the determination was carried out in the usual way, a blank determination being made. The accuracy was greatly increased by the addition of the buffer solution. E. M. P.

Differentiation of Natural and Artificial Orange Preparations by Formol Titration. A. Schrempf and E. Benk. (*Z. Unters. Lebensm.*, 1939, **77**, 39–46.)—The formol titration method used by Tillmans and Kiesgen (*Z. Unters. Lebensm.*, 1927, **53**, 132; Abst., ANALYST, 1927, **52**, 417) for the examination of natural and artificial citron juice was applied to the examination of products containing orange juice. To obtain the range for the natural product a number of samples of pure orange juice were prepared from peeled and unpeeled fruit. The juice (10 ml.) was nearly neutralised with aqueous sodium hydroxide solution and made faintly alkaline to phenolphthalein by titration with *N*/10 sodium hydroxide solution. A 40 per cent. solution of formaldehyde was neutralised to phenolphthalein, 10 ml. were added to the neutralised juice, and titration with *N*/10 sodium hydroxide was continued until the original faintly alkaline end-point was again reached. The number of ml. of *N*/10 alkali used in the final titration of 10 ml. of juice is the formol number. The range for the juice from peeled fruit was 2·05 to 2·9 and for juice from unpeeled fruit 1·7 to 2·15. Since many of the manufactured products are highly coloured with coal-tar dyes, which interfere with the formol titration both by obscuring the end-point and by reaction of their constituent amino groups, it is necessary to remove the dye by means of animal charcoal. The following procedure is recommended:—The beverage (100 ml.) or syrup or concentrate (100 ml. of a 10 per cent. dilution) is treated with animal charcoal and filtered. The clear colourless filtrate is almost neutralised to phenolphthalein with *N*/4 to *N*/1 sodium hydroxide solution according to its degree of acidity, and concentrated on the water-bath to 20 ml. When cold it is titrated to a faint pink colour with *N*/10 sodium hydroxide solution, 10 ml. of neutralised formalin are added, and the liquid is again titrated with *N*/10 sodium hydroxide solution. The final titration is calculated to 10 g. of syrup or 100 ml.

of diluted beverage. Since commercial orange syrup or concentrate contains about 35 per cent. of juice of sp.gr. 1·05, the formol value determined with 10 g. of syrup may be converted into the formol value for 10 ml. of juice by multiplying by 3. According to Tillmans, the range for citron juice is 2·1 to 2·6; the authors found a range of 1·7 to 2·9 for orange juice. The following examples indicate the value of the method as a means of distinguishing natural from artificial products. Orange syrups prepared from pure orange juice gave a formol number of 2·1 to 2·85; orange syrups prepared from the whole fruit including the peel gave 1·8 to 1·95; authentic commercial products gave 1·8 to 2·55; a number of commercial specimens, some admittedly not authentic, gave 0·3 to 1·2. All the above-mentioned figures are calculated to 10 ml. of juice, the actual experimental titration figures being one-third of the recorded figure. Aqueous and alcoholic extracts of orange peel (1 part of peel to 1 part of solvent) were prepared. The values for 10 ml. of extract were 0·8 to 0·9 (aqueous) and 0·7 to 0·85 (alcoholic). A syrup prepared with this extract gave a formol number of 0·25 ml. per 10 g. (0·75 ml. per 10 ml. of juice) and bore a close resemblance to certain commercial products which did not claim to be more than "orange flavoured." An artificial effervescing orangeade gave an average formol number of 0·1 ml. per 100 ml. A product prepared by tenfold dilution of genuine syrup gave a formol number of 0·6 ml. per 100 ml. Although the determination of the ash of the products was found to be of little value owing to variation in the mineral-content of local water supplies, and the determination of the phosphate-content was subject to large experimental errors, these determinations provided useful confirmation of opinions based on the formol number. A. O. J.

Determination of Stearic Acid in Fats. A. Heiduschka and W. Böhme. (*Z. Unters. Lebensm.*, 1939, **77**, 33–38.)—In the method of Hehner and Mitchell (ANALYST, 1896, **21**, 36) the stearic acid content of a mixture of fatty acids is determined by dissolving the acids in a warm alcoholic solution of pure stearic acid saturated at 0° C., cooling the solution to 0° C., and determining the amount of stearic acid which separates. Examination of the principle of this method revealed two difficulties: the stearic acid remaining in solution at 0° C. depends upon the initial concentration of the solution and its solubility is influenced by the presence of other acids. Varying amounts of a mixture of pure stearic and palmitic acids of known composition were subjected to this process and by comparison of the amounts of stearic acid found with those known to be present a correction table was constructed by means of which the stearic acid content of a mixture of fatty acids could be determined to within 1 per cent. If the mixture contains acids soluble only with difficulty (*e.g.* arachidic and behenic acids) these are precipitated with the stearic acid and their amount must be deducted. In the re-examination of the method it was found that most of the sources of error could be eliminated by the use of a thermostat controlling the temperatures of the solution to within 0·1° C., and the construction of such an instrument is described. The saturated solution of stearic acid was prepared by dissolving 4·500 g. of the pure acid in warm 99 per cent. alcohol and diluting the solution with alcohol to 1 litre at 20° C. The fatty acid mixture (0·5 g.) is dissolved in 100 ml. of this solution in a 200-ml.

flask immersed for a short time in boiling water. The flask is then connected with a stirring device and placed in the thermostat in which its temperature is maintained at 0° C. for 6 hours. The precipitated stearic acid is collected on a paper disc (No. 604, Schleicher and Schüll) in a Buchner funnel with gentle suction. On the filter-paper is a glass cylinder held against the paper by means of three hooked spiral springs, the object of which is to prevent the precipitate from settling on the sides of the funnel. The residue of stearic acid in the flask and on the stirrer is not removed, since both flask and stirrer form part of the apparatus subsequently used for extraction of the stearic acid. The filter-cake is sucked dry, 30 ml. of ether are placed in the empty flask, which is closed by a stopper carrying a glass "tulip" which in turn is connected with a reflux condenser. The filter with the stirrer and the glass cylinder are placed in the "tulip" and the ether in the flask is gently boiled. Extraction is usually complete in 5 minutes. After removal of the ether by evaporation, the flask is dried at 100° to 105° C. and weighed. The accuracy of the method is indicated by the agreement between parallel determinations. For exact determinations the final result is corrected by means of the table. The method was applied to the determination of the stearic acid content of pigs' fat and beef-fat. The percentage amounts of solid fatty acids found for the beef-fats by the lead salt and ether method were:—breast fat, 41·0; back fat, 40·0; kidney fat, 54·0. The amounts of stearic acid found were:—breast fat, 7·5; back fat, 11·0; kidney fat, 27·0 per cent. For pigs' fat the amounts of total solid acids were:—breast fat, 32·5; abdominal fat, 38·0; kidney fat, 53·0. The amounts of stearic acid found were:—breast fat, 12·0; abdominal fat, 13·5; kidney fat, 30·0. The differences between the amounts of stearic acid and of the total fatty acids were taken as palmitic acid. A. O. J.

Cycad Seed and Nigaki Fruit-coat Oils. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1938, 41, 319B–320B.)—The shell of Cycad seed, obtained from the Okinawa Islands, contained 8·29 per cent. of moisture and 21·44 per cent. of oil, and the kernels 30·50 per cent. of moisture and 0·50 per cent. of oil. The oils (obtained by extraction with ether) had the following properties and constants: —(*a*) *Shell Oil.*—At 23° C. this was an orange-coloured viscous liquid containing fine crystals; it became clear at about 39°; d_4^{45}, 0·8919; n_D^{20} (determined in liquid state), 1·4653; acid value, 48·2; saponification value, 196·6; iodine value (Wijs), 59·0; unsaponifiable matter, 2·54 per cent. The fatty acids became soft at 23° C. and melted at 45–46° C.; neutralisation value, 203·6; iodine value, 59·8. The bromide test gave no precipitate in ether and only a slight one in petroleum spirit. The lead salt and alcohol method of separation yielded 42 per cent. (diff.) of solid acids (m.p. 57–58° C., neutralisation value 213·9, iodine value 12·1), and 58 per cent. of liquid acids (n_D^{20} 1·4640, neutralisation value 195·6, iodine value 101·2). The acids were chiefly palmitic and oleic, with a small amount of linolic. The unsaponifiable matter, a yellow-orange viscous substance, contained carotinoid compounds (*cf.* Nishida, *J. Soc. Agric. Chem.*, 1937, 13, 89). (*b*) *Kernel Oil.*—At 23° C. this was an orange-yellow liquid, d_4^{30}, 0·9293; n_D^{20}, 1·4740; acid value, 8·7; saponification value, 173·2; iodine value (Wijs), 73·6.

Nigaki Fruit.—Oil from entire Nigaki fruit has previously been examined (cf. *Rep. Tokyo Imp. Ind. Res. Lab.*, 1931, **26**, 45; *Bull. Chem. Soc. Japan*, 1933, **8**, 161); it contains petroselinic acid. The fruit-coats (excluding hard endocarp) of two specimens from Chôsen, Korea, contained about 50 to 60 per cent. of oil. The oils (1) and (2), extracted with ether from the corresponding specimens, differed considerably in properties, as follows:—*Oil* (1).—At ordinary temperatures this was a soft brownish yellow-orange mass with slight fluorescence; d_4^{30}, 0·9351; n_D^{80}, 1·4670; acid value, 52·3; saponification value, 206·9; iodine value (Wijs), 62·6; acetyl value, 33·5; unsaponifiable matter, 2·97 per cent.; petroleum-spirit-insoluble (resinous) 0·50 per cent. The fatty acids were brownish-yellow and crystalline; m.p., 47–48° C.; neutralisation value, 213·4; iodine value, 57·6; bromide test: no precipitate in ether, 7·6 per cent. in petroleum spirit (linolic tetrabromide, m.p. 113–114° C.). The lead salt and alcohol method of separation yielded 46 per cent. (diff.) of solid acids (neutralisation value 201·8, iodine value 14·5) and 54 per cent. of liquid acids (neutralisation value 187·1, iodine value 112·4). The acids were chiefly palmitic and oleic, with a little linolic, smaller amounts of C_{12} or C_{14} acids or both and of acids higher than C_{18}, and some acidic resinous substance. *Oil* (2).—This was a yellowish-orange liquid with a small deposit of solid matter; it was slightly fluorescent; d_4^{20}, 0·9287; n_D^{20}, 1·4712; acid value, 17·5; saponification value, 199·9; iodine value (Wijs), 81·7; acetyl value, 23·6; unsaponifiable matter, 2·60 per cent., petroleum-spirit-insoluble (resinous), 0·85 per cent. The fatty acids contained approximately 3 per cent. of petroleum-spirit-insoluble matter. Petroselinic acid appeared to be absent from the fruit-coat; the unsaponifiable matter, a yellow viscous solid, contained sterol.

E. B. D.

Fatty Acids and Glycerides of Solid Seed Fats. VII. Dika Fat. W. J. Bushell and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1939, 58, 24–26.)—The kernels of *Irvingia gabonensis* (dika) used in this investigation were obtained from Sierra Leone and yielded 61 per cent. of fat with saponification equivalent 222·6; iodine value 1·8, and unsaponifiable matter 0·4 per cent. The component fatty acids (as per cent. mol.), calculated from the fractionation data, consisted of *n*-decoic, 3·8; lauric, 61·6; myristic, 30·8; palmitic, 1·6; stearic, 0·8; oleic, 1·4. Other recorded analytical data for *Irvingia gabonensis* show variations in iodine values from 2·1 to 9·8, and in saponification equivalents from 224·1 to 232·2. It is evident that there is more than one variety of *Irvingia gabonensis*, and the present sample was one of very low oleic acid content. Further, the seed fats of *Irvingia barteri* (Nigeria) and *Irvingia oliveri* (Cochin China) appear to be closely similar, but differ from the fat of *Irvingia gabonensis* in that their component acids include about 40 per cent. of lauric and 55 per cent. of myristic acid. The component glycerides of the dika fat were calculated after systematic crystallisation from acetone and oxidation of some of the fractions with potassium permanganate and determination of saponification equivalents. The calculation was only approximate owing to the presence of small proportions of mixed glycerides in which very small proportions of palmitic, stearic and oleic acids were combined as minor components. It may, however, be safely assumed that about two-thirds of the fat consist of dilauro-myristin, and also that this proportion and the probable approximate proportions of laurodimyristin and of some of the minor components (including the mono-oleo-glycerides of fractions 4 and 7, corresponding with about 6 per cent. of the whole fat, or three times the molar proportion of oleic acid in the component acids) accord with the close operation of the "even distribution" rule in the component glycerides of this fat. D. G. H.

Active Principles of *Cannabis Indica* Resin. T. S. Work, F. Bergel and A. R. Todd. (*Biochem. J.*, 1939, **33**, 123–127.)—The resin obtained from a sample of Indian hashish was esterified with *p*-nitrobenzoyl chloride. Cannabinol *p*-nitrobenzoate crystallised out from the solution of the crude ester in petroleum spirit; it had m.p. 160° C. On being hydrolysed it gave an almost colourless oil that yielded a crystalline acetate, m.p. 75° C. The cannabinol was non-toxic to rabbits when injected in doses less than 2 mg. per kg. body-weight, but was highly toxic in doses in excess of this. It did not induce corneal anaesthesia (Gayer test). The resin obtained by hydrolysis of the non-crystalline *p*-nitrobenzoates was also tested on rabbits. It had no effect in doses less than 1 mg. per kg. body-weight, but in doses exceeding that amount it produced sleep and loss of the corneal reflex. Doses in excess of 5 mg. per kg. body-weight were lethal. By chromatographic adsorption of the non-crystalline *p*-nitrobenzoates a fraction was obtained giving a positive Gayer test in a dose of 0·25 mg. per kg. body-weight. F. A. R.

Constituents of the Seeds of *Cleome viscosa*. M. P. Gupta and S. Dutt. (*J. Indian Chem. Soc.*, 1938, **15**, 532–536.)—*Cleome viscosa*, Linn. N.O. *Capparidae*, is a common plant in tropical India and Ceylon, and is called Hurhur or Hulhul or Kampute in Hindustani and Hurhuriya in Bengali. *Cleone pentaphylla*, already examined (Misra and Dutt, *Proc. Nat. Inst. Sci. India*, 1937, **3**, 45), is known by the same name in Hindustani, and the two species are much confused. The seeds are said to be anthelmintic, rubefacient and vesicant, and are regarded as much superior to mustard seed and equal to European mustard. The whole plant, according to O'Shaughnessy (Kirtikar and Basu, *Indian Medicinal Plants*, 1918, **1**, 98), is used as a counter irritant and blistering agent in Cochin China, and in the United States the roots are said to be used as a vermifuge. A new acid, viscosic acid, and a new flavone, viscosin, have now been isolated from the seeds. Benzene extraction of the seeds yielded 36·59 per cent. of a reddish-yellow oil from which some waxy material separated. The oil deposited a crystalline material found to consist of myristic, palmitic and the new viscosic acid. This acid was obtained from the crystalline deposit by washing with benzene, drying and taking up with ether. The fraction insoluble in ether was crystallised twice from ethyl alcohol and then repeatedly from methyl alcohol and a yield of 0·1 per cent. of white crystalline needles, m.p. 97° C., was obtained. Viscosic acid does not reduce Fehling solution, dissolves in cold conc. sulphuric acid, gives no colour with ferric chloride solution, and does not form oximes or acetyl derivatives. Its composition corresponds with the formula $C_{27}H_{52}O_3$, and it appears to be an unsaturated fatty acid. On oxidation with dilute potassium permanganate it yields a dihydroxy acid, $C_{27}H_{54}O_5$, and has one double bond and an iodine value (Wijs) 22·5. On extracting the defatted seeds with boiling ethyl alcohol crystals were deposited which were found to be viscosic acid. The mother liquor was further concentrated, freed from moisture and extracted with petroleum spirit. The insoluble portion was dissolved in alcohol, and the solution was treated with excess of lead acetate. The lead salt was collected and decomposed in alcoholic suspension with hydrogen sulphide. On dilution with water tannins and a yellow substance were precipitated. The colouring matter was freed from tannins by extraction with boiling water and recrystallised several times from water and then from aqueous methyl alcohol. Finally, the pale yellow hexagonal plates were crystallised from aqueous *iso*propyl alcohol. The viscosin obtained darkened at 285° C. and melted with decomposition at 294–295° C. Viscosin has a composition corresponding with the formula $C_{16}H_{12}O_6$ and contains no water of crystallisation. It gives a dark green colour with alcoholic ferric chloride solution, forms a triacetyl derivative and contains one methoxy group. It is, in fact, a monomethoxytrihydroxy flavone. A 1 per cent. alcoholic solution had a well-defined absorption band between 410 and 462$m\mu$ with absorption maximum at 442·5$m\mu$. A study of the physiological action of viscosin is in progress.

D. G. H.

Microchemical Reactions for Acedicon. F. Amelink. (*Pharm. Weekblad*, 1939, **76**, 74–77.)—Acedicon is an isomer of acetylated codeine, differing from it in the position of the double bond, which is attached to the same carbon atom as the acetylated enolic hydroxyl group. It is prepared synthetically, has a m.p. of 152° to 153° C., and is sold in the form of the hydrochloride (by Boehringer). The following tests were evolved with the object of fitting it into a general scheme for the microchemical identification of alkaloids (*Schema zur Mikrochemischen Identifikation von Alkaloiden*, Amsterdam, D.B. Centen); most of the crystal-forms are illustrated by drawings in the paper abstracted. Platinic chloride produces a pale yellow precipitate, which in acid solutions forms doubly-refracting globules, 8 to 15μ in size, characteristic in appearance and grouping under the low powers of the microscope. In neutral solutions these are similar but larger (50μ), and form star-shaped clusters of radiating deformed needles. Sodium iodide is without effect on the reaction, which is definite with 0·1 per cent. solutions of acedicon. Gold chloride in neutral solution produces an abundant precipitate of strongly doubly-refracting, thin, flat prisms which appear pale green by transmitted light, and form star-shaped groups 90 to 270μ in size. They are dichroic (light yellow to colourless) and *d*-rotatory, and the reaction is unaffected by the presence of sodium bromide and is given by 0·1 per cent. solutions. Mercuric chloride in acid solution produces a white precipitate of droplets, which on warming, scratching and cooling form star-shaped groups of tree-like branched needles, 130 to 500μ in size. On adding a drop of water and scratching vigorously the crystals grow, forming strongly doubly-refracting, *d*-rotatory prisms (size 50 to 150μ), grouped in long, almost rectangular block-shaped aggregates; sensitiveness, 0·5 per cent. Potassium ferrocyanide gives no reaction in the presence of acid, but in a neutral medium a precipitate is formed (particularly if the liquid is warmed and the microscope slide scratched while it is cooling), consisting of groups in the form of stars and sheaves of thin, light-brown strongly doubly-refracting, *d*-rotatory needles, 120 to 700μ in size when produced from 1·0 per cent. solutions; sensitiveness, 0·2 per cent. Potassium ferricyanide gives a negative reaction in both acid and neutral solutions; Dragendorff's reagent (modified form, *loc. cit.*, p. 7) gives a brown precipitate which is useless as a means of identification. Potassium hydroxide solution produces a precipitate of white droplets. Ammonium dichromate forms star-shaped groups of strongly doubly-refracting brown crystals, 40 to 250μ in size, from cold neutral 1 per cent. solutions, but 0·5 per cent. solutions give indefinite results. Sodium anthraquinone-β-sulphonic acid produces abundant crystals from neutral 0·1 per cent. solutions. These, however, are not particularly characteristic, unless the solution is subsequently warmed, when fine, strongly doubly-refracting, *d*-rotatory needles are deposited (size, 70 to 130μ). Sodium carbonate may be used to "salt out" the base from neutral 0·1 per cent. solutions. In the cold, droplets result, which form star-shaped groups (size, 150μ) of crystals with brush-like ends; on scratching, groups in the form of stars and sheaves (size, 20 to 70μ) are obtained. Sodium bicarbonate behaves similarly, but only with solutions stronger than 0·5 per cent., and the crystals are star-shaped groups of prisms (size, 300 to 800μ). Sodium phosphate solution (Dutch Pharmacopoeia, Ed. V), however, is the best "salting out" agent; it produces sheaf-shaped groups of prisms (about 30μ in size at first, but growing to 130μ) from 0·2 per cent. solutions. In all three tests the crystals of the base are doubly-refracting and *d*-rotatory. Conc. sulphuric acid and Erdmann's reagent produce a pale yellow colour; Frohde's reagent, olive green to yellow; Marquis' reagent, yellow-brown, changing through red-violet to blue-purple. The platinic chloride, mercuric chloride, sodium anthraquinone-β-sulphonic acid and gold chloride reagents are specific for acedicon in dilute solutions, and the two last are considered the best. J. G.

Biochemical

Micro-determination of Oxyhaemoglobin, Methaemoglobin and Sulphaemoglobin in a Single Sample of Blood. K. A. Evelyn and H. G. Malloy. (*J. Biol. Chem.*, 1938, **126**, 655–662.)—When sodium cyanide is added to a solution of methaemoglobin, this is converted into cyano-methaemoglobin and the characteristic absorption band at 635*m*μ is almost completely eliminated; the resulting change in absorption at 635*m*μ is directly proportional to the concentration of methaemoglobin. The 620*m*μ absorption band of sulphaemoglobin is unchanged by the addition of cyanide, and thus the concentration of sulphaemoglobin is proportional to the absorption at 620*m*μ after the addition of cyanide, but a correction has to be applied for the small absorption of oxyhaemoglobin and cyano-methaemoglobin at 620*m*μ. The concentration of oxyhaemoglobin can be calculated by difference. Fresh whole blood (0·1 ml.) is added to 10 ml. of $M/60$ phosphate buffer of *p*H 6·6 in a colorimeter tube. The solution is allowed to stand for 5 minutes, and a reading (L_1) is made with filter 635 after the galvanometer has been adjusted to 100 with a blank tube containing water only. One drop of a solution made by mixing equal parts of 10 per cent. sodium cyanide solution and 12 per cent. acetic acid is then added and after 2 minutes a second reading (L_2) is made with the same filter and blank tube. The difference (L_1–L_2) is proportional to the concentration of methaemoglobin. The solution is cleared by the addition of one drop of conc. ammonium hydroxide and a third reading (L_3) is made with filter 620 and a blank tube containing water only. Finally, 2 ml. of the solution are pipetted into a second colorimeter tube containing 8 ml. of $M/15$ phosphate buffer of *p*H 6·6 and 1 drop of 20 per cent. potassium ferricyanide solution. The tube is allowed to stand for 2 minutes to allow all the oxyhaemoglobin to be converted into methaemoglobin. After the addition of 1 drop of 10 per cent. sodium cyanide solution, the mixture is allowed to stand for another 2 minutes to convert the methaemoglobin into cyano-methaemoglobin and a fourth reading (L_4) is then made with filter 540 and a blank tube containing 10 ml. of water and 1 drop each of 20 per cent. potassium ferricyanide solution and 10 per cent. sodium cyanide solution. Then

concentration (g. per 100 ml.) of total haemoglobin (T) $= \dfrac{100 \times L_4}{2{\cdot}38}$

„ („ „) „ methaemoglobin (M) $= \dfrac{100(L_1 - L_2)}{2{\cdot}77}$

„ („ „) „ sulphaemoglobin (S) =

$$\frac{1000 \times L_3 - (8{\cdot}5 \times M + 4{\cdot}4 \times T)}{100}$$

„ („ „) „ oxyhaemoglobin $= T - (M + S)$.

The numerical values of the calibration constants which appear in the above equations only hold good for the particular colorimeter used. The first equation is not strictly accurate when sulphaemoglobin is present, and a correction equal to 0·22 × S must be added to the value of T. The error in the determination of total haemoglobin is about 0·2 g. per 100 ml. in the absence of sulphaemoglobin and 0·4 g. when this is present. The error in estimating methaemoglobin is less than 0·2 g. per 100 ml. and that for sulphaemoglobin probably not much higher. Little interference was encountered from extraneous pigments present. F. A. R.

Colorimetric Method for the Determination of Inulin in Blood Plasma and Urine. K. Steinitz. (*J. Biol. Chem.*, 1938, **126**, 589–593.)—Inulin is one of the most satisfactory substances for the determination of glomerular filtration and an accurate method of estimating inulin in blood plasma and urine is therefore highly desirable. The method proposed is that used by Roe (*cf.* ANALYST, 1934, **59**, 835) for the estimation of fructose, as it was found that inulin was completely hydrolysed by conc. hydrochloric acid in the time taken for full development of the fructose colour (8 minutes).

The estimation was carried out according to the procedure adopted by Roe, except that with plasma determinations standard solutions of fructose were prepared containing 0·5, 1, 2 and 3 mg. per cent. in saturated benzoic acid solution. For the estimation in urine, dilutions of 5, 10, 20 and 30 mg. per cent. in 1 per cent. acetic acid with 1 per cent. sublimate was prepared. The colour of the unknown solution was compared in a colorimeter with that of the standard solution that most nearly matches it, a green filter transmitting at 510$m\mu$ being used. F. A. R.

Study of the Passage of Fatty Acids of Food into Lipins and Glycerides of the Body, using Deuterium as an Indicator. B. Cavanagh and H. S. Raper. (*Biochem. J.*, 1939, **33**, 17–21.)—A fat containing 4 to 5 atoms per cent. of deuterium was fed to rats, and the distribution of the deutero-fatty acids in the "lipin" (acetone-insoluble) and "glyceride" (acetone-soluble) fractions of liver, kidney, brain and blood was determined 6, 10 and 24 hours afterwards by combustion of the fats and measurement of the density of the water so formed. At the end of 6 hours about 26 per cent. of the plasma glyceride, 18 per cent. of the liver glyceride, 14 per cent. of the liver lipin fatty acids, and 2·5 per cent. of the kidney glyceride were derived from the deutero-fat administered, which indicates a selective intake of fat from the blood by the liver soon after its absorption, the lipins of the liver also participating in this phenomenon. The brain and adipose tissue contained only traces of deuterium. At the end of 24 hours, the amount of deuterium in the glyceride fraction of the liver and of the plasma had decreased markedly, but the deuterium-content of the lipoid fraction of the liver, the kidney and the brain showed comparatively little change. These results emphasise the important part played in fat metabolism by the liver lipins. F. A. R.

Researches on the Protoplasm of Green Plant-cells. I. Isolation of the Chloroplasts of Spinach-leaves. W. Menke. (*Z. physiol. Chem.*, 1938, **257**, 43–48.)—Fresh spinach-leaves were ground in a roller-mill so as to disintegrate the tissue without destroying all the chloroplasts, and the press-juice was centrifuged. The sediment, containing cell-fragments and unchanged chloroplasts, was suspended in a buffer-solution and again centrifuged, first at a low speed to remove coarse particles, and then at a high speed to separate the chloroplasts. These were purified by further fractional centrifuging, and finally dried *in vacuo* after being frozen. The lipoid-content of the material was estimated by extraction first with ether and then with a mixture of ether and alcohol; the protein-content was estimated by multiplying by 6·25 the nitrogen-content determined by the micro-Kjeldahl method; the ash was determined by ignition. The percentages of protein, lipoid and ash in the chloroplasts and in a "chloroplast-substance" previously prepared by extraction (*Z. Bot.*, 1937, **32**, 273) were respectively: 47·7, 56·4; 37·4, 31·9; 7·8 and 4·7. It is concluded from the lower protein-content of the chloroplasts that the extract previously made was contaminated with some 15 per cent. of "cytoplasm-substance." The protein of the chloroplast, unlike that of the cytoplasm, which is a glutelin, is soluble to the extent of only about 20 per cent. in water, dilute salt solutions or dilute acid or alkali. When the fat-free chloroplasts were extracted with water made very slightly alkaline, a protein containing phosphorus was extracted and could be precipitated by adding acid; this resembled a nucleo-protein. F. A. R.

Application of Schryver-Fosse Reaction to Tests for Oxalic Acid, Ascorbic Acid, Tartaric Acid and Uric Acid. M. Paget and R. Berger. (*Compt. rend.*, 1938, **207**, 800–802.)—*Detection and Determination of Small Amounts of Oxalic Acid.*—Oxalic acid is reduced by means of zinc and hydrochloric acid to glyoxylic acid, which is then determined colorimetrically by the Schryver–Fosse reaction with phenylhydrazine. To 2 ml. of the solution, containing 5 to 70 mg.

of oxalic acid per litre, is added 1 ml. of *N* hydrochloric acid and a piece of zinc foil. The liquid is stirred electrically at 275 r.p.m. for 30 minutes. A 2-ml. portion is transferred to a Pyrex tube, and 2 drops of a 1 per cent. solution of phenylhydrazine hydrochloride solution are added. The tube is heated in boiling water for 2 minutes and cooled, 1·8 ml. of conc. hydrochloric acid and 2 drops of hydrogen peroxide (10 vol.) are introduced, and the tube is kept in darkness for 10 minutes to allow the colour to develop. The colour is matched colorimetrically against a standard prepared by treating an oxalic acid solution of known strength in an exactly similar manner. Sensitiveness of test: 1/200th mg. of oxalic acid. The cations Na, K, NH_4, Li, Ba, Sr, Ca, Mn, Fe and Zn do not interfere. *Ascorbic Acid.*—This acid is oxidised, yielding a mixture of threonic acid and oxalic acid, as follows: To 1 ml. of the ascorbic acid solution are added 2 drops of conc. sulphuric acid and 2 drops of 3 per cent. potassium permanganate solution. After 2 minutes the solution is decolorised by the addition of hydrogen peroxide. The oxalic acid in the solution is then determined as described above. Sensitiveness: 1/100th–2/100th mg. of ascorbic acid. *Tartaric Acid.*—Oxidation of the solution as for ascorbic acid yields a mixture of glyoxylic acid (small amounts), oxalic acid and butane-dione-2·3-dioic acid. The oxalic acid may be tested for as described above. Other hydroxy-carboxylic acids may give similar reactions. *Uric Acid.*—Heating a solution of uric acid made alkaline with sodium carbonate yields allantoic acid, which is capable of being tested for by the Schryver–Fosse reaction. S. G. C.

Determination of Ascorbic Acid in Urine with the Photoelectric Colorimeter. K. A. Evelyn, H. T. Malloy and C. Rosen. (*J. Biol. Chem.*, 1938, **126**, 645–654.)—Estimation of the ascorbic acid content of urine by titration with 2 : 6-dichlorophenolindophenol, according to the usual procedure, gives high results because other substances that reduce the dye are present in urine. A somewhat empirical method has been devised for reducing the errors introduced by the presence of these interfering substances, based on the observation that whilst ascorbic acid reduces the dye almost instantaneously, other substances react much more slowly. Nine ml. of an aqueous solution of dichlorophenolindophenol are added from a specially prepared rapid delivery (1 sec.) pipette to 1 ml. of 5 per cent. acetic acid in a colorimeter tube and the colour is measured immediately in a photoelectric colorimeter (filter 520) after the galvanometer has been adjusted to 100 with a tube containing water only. The corresponding reading (L_1) is noted. The galvanometer is then adjusted to 100 with a blank tube containing 9 ml. of water and 1 ml. of urine acidified with 5 per cent. (by volume) of glacial acetic acid. Nine ml. of the dye solution are introduced into another tube containing 1 ml. of the acidified urine, from the special pipette, and the galvanometer reading is recorded 5, 10, 20 and 30 seconds after the addition of the dye began. These readings are plotted and the smooth curve obtained is produced backwards to cut the ordinate. The galvanometer reading so extrapolated (L_2) to zero time is noted. Then the concentration (X) of ascorbic acid in mg. per 100 ml. of acidified urine is calculated from the equation:

$$X = \frac{10{\cdot}8\,(L_1 - L_2)}{A}$$

where 10·8 is the calibration constant of the particular instrument used obtained by measurement of solutions of pure ascorbic acid and A is the volume (ml.) of acidified urine used in the test. The equation is accurate only when the proportion of the dye solution to urine is 9 : 1. Whereas by the usual method of titrating with the dye, the presence of sodium thiosulphate and cysteine often leads to too high a value for the ascorbic acid content of solutions, the photoelectric method gives results much more closely in agreement with the theoretical values. In a number of normal urines that were examined the ratio of titrimetric to photoelectric values varied from almost 1 : 1 to 10 : 1 and more, and considerable doubt is thrown upon the urinary excretion test used to detect vitamin C subnutrition. An attempt was also made to improve the accuracy of the method still further by a preliminary purification of the urine, and this was found to be most conveniently effected by precipitation of interfering substances with barium acetate (*cf.* P. J. Drumm, H. Scarborough and C. P. Stewart, *Biochem. J.*, **1937**, **31**, 1874; ANALYST, 1938, **63**, 58). F. A. R.

Catatorulin Test for Vitamin B$_1$. R. A. Peters. (*Biochem. J.*, 1938, **32**, 2031–2036.)—An improved catatorulin test for estimating vitamin B$_1$ is described, the chief improvement being the use of sodium pyruvate instead of lactate as substrate. A small amount of the minced brain (cerebrum and optic lobes) of avitaminous pigeons is suspended in Ringer-phosphate solution (*p*H 7·3) containing 6 mg. of sodium pyruvate. Triplicate estimations, if possible, of the oxygen uptake of the minced brain are made after the addition of 0, 0·25 and 0·5γ of the vitamin. The tubes are allowed to stand at room temperature for about 10 minutes before filling them with oxygen, and the volume of oxygen absorbed by the three lots of tissue during the period 1 to 2 hours is measured and then plotted against the amount of vitamin added. The resulting curve usually approximates to a straight line, and from it the amount of vitamin B$_1$ present can be calculated, since the value of the oxygen uptake of the pure vitamin under the same conditions is known. The errors involved in the estimation are variable, the results from some brains having to be discarded. F. A. R.

Estimation of Vitamin B$_1$ in Blood. H. M. Sinclair. (*Biochem. J.*, 1938, **32**, 2185–2199.)—The claim made by Meiklejohn (*Biochem. J.*, 1937, **31**, 1441), *viz.* that the estimation of vitamin B$_1$ in blood by its effect on the growth of the mould *Phycomyces blakesleeanus* "provides a quantitative estimate of the true vitamin B$_1$ content of the blood," is subjected to examination, and his results are not confirmed. It has now been shown that hydrolysed casein is a more satisfactory source of nitrogen than the asparagine used by Meiklejohn, and that the marked adjuvant action of blood in the presence of asparagine is due to sources of nitrogen in the blood; Meiklejohn's medium was also deficient in salts. A further cause of the adjuvant action of blood is its buffering action, which allows the fungus to continue to grow for longer than it otherwise would; the addition of calcium carbonate invariably produces an increase in growth in solutions without blood. If consistent results are to be obtained, care must be taken to control such factors as the temperature of autoclaving and the length of time the blood is stored; the variations that occur are probably due to destruction of adjuvant factor in the first case and to an increase as a result of autolysis in the second. Substances other than vitamin B_1 that act as growth factors for the fungus are: bios, break-down products of vitamin B_1 (producing growths much greater than those obtained with excess of vitamin B_1) autoclaved marmite, autolysed yeast and "Peter's eluate." Indole, amongst other substances, inhibited growth. It is concluded that when the possible sources of error are borne in mind and controlled as far as possible, the method is valuable for comparing the apparent vitamin B_1 contents of different samples of blood. F. A. R.

Occurrence of Vitamin B_2 (Lactoflavin). Part I. Vitamin B_2 in Muscle. J. Schormüller. (*Z. Unters. Lebensm.*, 1939, **77**, 1–18.)—In order to determine lactoflavin in extracts of animal tissue it was converted by irradiation in alkaline solution into lumiflavin and the colour of this was measured photometrically. It is necessary to distinguish between the determination of total flavins and the determination of free flavins and the flavin combined with protein (yellow enzyme). The determination of total flavins was made by the procedure of v. Euler and Adler (*Z. physiol. Chem.*, 1934, **223**, 105) by repeated extraction with aqueous 60 to 80 per cent. acetone or with boiling water. The combined extracts were concentrated *in vacuo* and purified with ether, chloroform or petroleum spirit. Irradiation, chloroform extraction and colorimetric measurements followed the procedure of Kuhn and his collaborators (*Ber.*, 1934, **67**, 1455). Often, in spite of repeated purification, the chloroform solution was coloured brown. In these instances, before the photometric measurement, the extract was subjected to chromatographic separation by means of a layer of aluminium oxide, the intensely coloured lumiflavin being separated by a mixture of 100 parts of pyridine, 10 parts of methyl alcohol and 10 parts of chloroform. Complete separation of lumiflavin from non-fluorescent impurities was thus effected. Lumiflavin, purified by recrystallisation from absolute alcohol, appeared under the microscope as fine tufts of needle crystals. Its m.p. (uncorr.) was 237 to 238° C. and, by the method of mixed m.p., muscle lumiflavin was found to be identical with liver-lumiflavin. To separate the flavins of low molecular weight (lactoflavin and its phosphoric ester) from the flavin combined with colloidal carriers (yellow enzyme) the aqueous extracts were dialysed in cellophane tubes immersed in distilled water for 16 hours at 3° C. The two fractions were then converted into lumiflavin and analysed. Lactoflavin was separated from its phosphoric ester by extraction of the aqueous solution with benzyl alcohol in which the unesterified compound is soluble (Emmerie, *Nature*, 1938, **141**, 416). The lactoflavin-content (γ per 100 g. of dry material) of various kinds of muscle fibre is as follows:—lean beef, 155·6 to 222·7; lean veal, 280·8 to 291·0; lean pork, 348·6 to 374·6; lean mutton, 268·1; fat mutton, 399·2; lean horse flesh, 425·3 to 433·9; hen (total muscle), 199·8; dog (total muscle), 179·4; Liebig's meat extract (original undried substance), 1932 to 2071. Little variation in vitamin B_2 content was found in corresponding portions of animals of the same species. A comparison of the figures obtained by biological methods and by chemical analysis shows that, although the amounts found by the two methods may vary widely, they give similar ratios for the distribution of the vitamin among different organs. Liver has from 10 to 15 times as much vitamin B_2 as muscle, and cow's heart-muscle has 7 times as much as lean beef. A considerable amount of man's daily requirement of vitamin B_2 (2 to 3 mg. of lactoflavin) is supplied by meat, especially by such organs as heart, liver and kidneys. An examination of the smooth muscle and mucous membrane of the cow's intestines showed that smooth muscle contains about 3 times and the mucous membrane of the intestine about 6 times as much lactoflavin as striped muscle. The muscle fibre of fresh-water and sea-water fish was found to be comparable with lean beef in vitamin-content, whilst turbot roe contains 16 times as much as cod-muscle. An experiment designed to imitate the ordinary boiling of meat showed that 70 per cent. of the flavin appears in the broth, and this accounts for the high vitamin B_2 content of meat extracts. An inverse relationship appears to exist between the lactoflavin-content and the glycogen-content of muscle. Tonic muscle with slow movement (*e.g.* smooth viscera-muscle and red leg-muscle) contains much lactoflavin and little glycogen. Non-tonic, quick-moving muscle (*e.g.* pale breast-muscle) is rich in glycogen and poor in lactoflavin. A. O. J.

New Method for the Isolation of α- and β-Tocopherols. A. R. Moss and J. C. Drummond. (*Biochem. J.*, 1938, **32**, 1953–1956.)—The saponification of wheat-germ oil and extraction of the unsaponifiable matter apparently effects a fourteen-fold concentration of the vitamin E present, but evidence has recently been accumulating to show that the concentration effected is in fact much smaller than this because of the sensitivity of the vitamin to alkali. Accordingly, an attempt was made to prepare a vitamin E concentrate by an alternative method. This was successfully done by chromatography. A 10 per cent. solution of wheat-germ oil in petroleum spirit was poured on to a column of alumina, but instead of the chromatogram being developed with fresh solvent, more of the solution was added until the band containing vitamin E reached almost to the bottom of the column. Three bands were formed: a pinkish-yellow zone which eventually passed through the column into the filtrate, a yellow zone which passed slowly down the column and tended to separate into two bands, and a deep orange yellow band which was adsorbed at the top of the column. After the column had been washed with petroleum spirit, the two bands of the yellow zone were separately eluted with a mixture of ether, benzene and methyl alcohol. They contained the vitamin E, and the concentrates so made were (together) some 14 times richer than the original oil. Both had absorption maxima at about 295*m*μ, but yielded only oily allophanates. After saponification, however, crystalline allophanates of β- and α-tocopherol were obtained from the upper and lower bands respectively. Two kg. of wheat-germ oil yielded 1 g. of α- and 0·75 g. of β-tocopherol allophanate.

F. A. R.

Colorimetric Determination of α-Tocopherol (Vitamin E). A. Emmerie and C. Engel. (*Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 1351–1358.)—The method of estimating vitamin E proposed by Karrer and Keller (*cf.* ANALYST, 1938, **63**, 835) was based on the reduction of gold chloride solution by the vitamin. It has now been found that, although tocopherol only slowly reduces ferric chloride alone, the reduction is much more rapid in the presence of *αα'*-dipyridyl, which immediately removes the ferrous ions formed. One ml. of a 0·2 per cent. alcoholic solution of ferric chloride (freshly prepared) is added to about 1 ml. of an alcoholic solution (containing 0·1 to 0·4 mg.) of tocopherol. The two solutions are mixed, 1 ml. of a 0·5 per cent. alcoholic solution of *αα'*-dipyridyl is added, and the solution is diluted to 25 ml. The red colour of the ferrous-dipyridyl complex is measured after 10 to 15 minutes by means of the Zeiss–Pulfrich photometer, screen 50 and a 1 cm. cell being used. A blank solution is prepared with ferric chloride solution and *αα'*-dipyridyl and placed in the other cell of the photometer. A standard curve is prepared by using *α*-tocopherol. Since carotene also reduces ferric chloride, allowance must be made for this in calculating the vitamin E contents of oils or concentrates that also contain carotene. A standard curve is constructed for carotene, and the conversion factor for carotene into tocopherol is calculated from it. In estimating the amount of vitamin E in oils, these are first saponified by heating with twice their volume of 2 *N* methyl alcoholic potassium hydroxide solution for 10 minutes in an atmosphere of nitrogen. The unsaponifiable matter is extracted with ether from the soap solution after dilution with water and then dissolved in alcohol. The results were in close agreement with those obtained by Karrer's method. F. A. R.

Quantitative Photometric Estimation of Vitamin E. M. Furter and R. E. Meyer. (*Helv. Chim. Acta*, 1939, **32**, 240–250.)—Both natural *β*-tocopherol and synthetic *d,l.-α*-tocopherol in alcoholic solution give deep red solutions on being treated with nitric acid, but the nature of the reaction is not known. The colour is not given by any substance with which synthetic or natural tocopherol is likely to be associated. Thus hydroquinone, xyloquinone, trimethyl hydroquinone, durohydroquinone and naphthoquinone, equilin and equilenin, tyrosine and *β*-carotene gave yellow solutions; phytol and phytyl bromide, ascorbic acid, androsterone and oestrone, phenol, *α*- and *β*-resorcylic acids and salicylic acid, glucose, starch and lactose gave colourless solutions. Wheat-germ oil was the only oil tested that gave a red colour, though castor oil gave a pale rose colour; linseed, sesame and cod-liver oils gave yellow solutions and arachis and olive oils colourless solutions. The reaction has been made the basis of a method of estimating vitamin E. The absorption spectrum of the coloured solution has a well-defined maximum at 467*mμ*, and the intensity of the absorption at this wavelength is strictly proportional to the concentration of the vitamin and to the thickness of the layer of solution. Moreover, the intensity did not decrease on standing for 24 hours. The estimation of tocopherol can be carried out with fair accuracy, the error involved seldom being greater than 3 per cent. The minimum quantity of material that can be estimated is 0·05 per cent. One to 5 mg. of material, containing not less than 0·3 mg. of tocopherol are weighed into a 25-ml. flask and dissolved in about 5 ml. of absolute alcohol. Alternatively a 5-ml. aliquot portion of an alcoholic solution of known strength is transferred to the flask. One ml. of pure conc. (65 per cent.) nitric acid is added from a burette, the flask being gently rotated during the addition. A small piece of porous pot is put into the flask, which is then fitted with a reflux condenser, and the contents are heated gently under reflux for 3 minutes, after which the flask is cooled and allowed to stand for 15 minutes. A little of the solution is transferred by means of a pipette to the 1-cm. cell of a Pulfrich photometer fitted with filter S47. A mixture of 83·5 per cent. (by volume) of absolute alcohol and 16·5 per cent. of conc. nitric acid is put into the other cell of the photometer. From the extinction value of the solution the vitamin E content is calculated by reference to a standard curve made with pure α-tocopherol. The two tocopherols give identical values.

One great advantage of the method over those previously described is that the estimation of vitamin E in oils can be done without saponifying them. A quantity of the oil (0·2 to 0·3 g.) is weighed into a 25-ml. flask and dissolved or suspended in 5 ml. of absolute alcohol. After the addition of 1 ml. of conc. nitric acid, the mixture is boiled for 3 minutes. On cooling, two layers form, the red colour being partitioned between them. The upper alcoholic layer is separated and filtered through a micro-filter funnel and the filtrate is made up to a volume of 6 ml. The lower oily layer is dissolved in 3 ml. of pure acetone, and the solution is poured through the filter used for clarifying the alcohol layer. The flask and filter are washed with 3 small portions of acetone, and the volume of the acetone solution is made up to 6 ml. The colour of each solution is measured in the photometer, the compensating cell being filled with a solution of the untreated oil in acetone when the colour of the acetone solution is measured. On reference to the standard curves, the sum of the extinction values gives the vitamin E content of the oil. F. A. R.

Investigations into the Method of Estimating Vitamin E. III. Relation between Dosage and Response to Vitamin E. A. L. Bacharach. (*Biochem. J.*, 1938, **32**, 2017–2023.)—Six groups of virgin rats reared on a vitamin E-free diet were given respectively 1, 2, 4, 8, 16 and 32 "units" of a vitamin E concentrate that had been stored in an atmosphere of nitrogen in sealed tubes. The number of rats in each group varied from 20 to 64. When the percentage of fertile rats ("fertility rate") in each group was plotted against the dose, a smooth curve resulted which flattened out very markedly at a fertility rate greater than 90 per cent. The curve affords a means of expressing the vitamin E content of oils and concentrates in terms of the "standard" concentrate, and if a fertility rate near to 50 per cent. results from the administration of a particular dose, the activity can be assessed with fair accuracy.

The amount of α-tocopherol required to produce 50 per cent. fertility ("mean fertility dose") was found to be 1·5 mg., and that of β-tocopherol rather over half this value; this latter estimate, however, is subject to a high degree of error. The mean fertility doses of three samples of wheat germ oil were found to be 280, 700 and 250 mg., and that of a concentrate prepared from the last-mentioned oil 15 mg. F. A. R.

Specificity of Vitamin E Activity. F. v. Werder, T. Moll and F. Jung. (*Z. physiol. Chem.*, 1939, **257**, 129–139.)—About 20 compounds more or less closely related to the tocopherols were prepared and tested for vitamin E activity. Durohydroquinone, pseudocumoquinone and their simple derivatives were either inactive or only slightly active when given in a 100 mg. dose. The compounds 2, 5, 7, 8-tetramethyl chroman, 2, 5, 7, 8-tetramethyl-6-hydroxy-chroman, 2, 4, 6, 7-tetramethyl-5-hydroxy-coumarone and 2, 4, 6, 7-tetramethyl-5-hydroxy-coumaran were inactive, as was also 6-desoxy-*d.l.*-α-tocopherol prepared by condensing phytyl bromide with 1, 2, 4-trimethyl-6-hydroxy-benzene in presence of zinc chloride. *d.l.*-α-Tocopherol was found to be active in a dose of 3 mg. in 22 out of 28 animals. F. A. R.

Bacteriological

Dark-ground Studies of Flagellar and Somatic Agglutination of *B. typhosus*. A. Pijper. (*J. Path. and Bact.*, 1938, **47**, 1–17.)—An account is given of dark-ground methods, in which the sun is used as the source of light, so that the flagella of *B. typhosus* and similar bacteria swimming in broth can be seen and photographed. *B. typhosus* and similar bacteria swim by means of a long tail. At rest, the tail unwinds itself into two somewhat broadly coiled spiral flagella which are attached approximately near the middle of the bacterium and take up a position at an angle to its long axis. When resuming activity the two flagella begin to revolve round their own axis, stretch and become twisted round one another at the rear end of the bacterium where they form the tail. The two flagella consist of a number of extremely thin threads as can be seen when they finally disintegrate. The traditional picture of peritrichous flagella is shown to be due to artifacts resulting from the drying of films. In "H" agglutination the tails and flagella become covered with a granular deposit, which finally completely covers and ensheathes them. The resulting stiff and thickened spiral structures become entangled with those of the other cells. In "O" agglutination the cells exert a real mutual attraction, the force acting in the direction of the long axis, so that they join up end to end and build up clumps which exhibit a regular pattern. Neither tails nor flagella take part in this process. D. R. W.

Destruction of Bacterial Spores. Low Temperature Sterilisation. C. E. Coulthard. (*Pharm. J.*, 1939, **142**, 79.)—Several previous papers on this subject from the bacteriological laboratory of Boots' Pure Drug Co. have been published (*cf.* ANALYST, 1937, **62**, 217). This paper records more recent work, the investigation coming under three principal headings: (1) The use of germicides to increase the bactericidal value of intermittent heating at 80° C.; (2) the use of germicides to increase the bactericidal value of (*a*) a short period of heating at 80° C., and (*b*) a relatively long period of heating at this temperature; (3) the use of germicides to increase the bactericidal value of heating at 100° C. Spore suspensions in dilute glycerin were made from soil and laboratory cultures of *B. mesentericus* and related organisms. These suspensions were distributed into bottles, heated to 80° C. to destroy vegetative cells and stored just above freezing-point. Five-ml. volumes of the various test solutions were distributed into vials, sown with spore suspensions, heated in water to the desired temperature and subsequently tested. The results of the experiments show that: (1) a large number of spores are viable after intermittent heating at 80° C. without antiseptics, a greatly reduced number are viable when 0·5 per cent. phenol or 0·3 per cent. tricresol is present, and usually none (but sometimes a few) remain viable when 0·25 per cent. of *p*-chloro-*m*-cresol is present; (2) after 1 hour's heating at 80° C. the addition of sufficient mineral acid to give a *p*H of about 2·25 is necessary for the destruction of spores; this is also effected by the addition of phenyl mercuric nitrate in concentration of 1: 5000 and nearly effected with concentration of 1: 10,000 to 1: 20,000. Experiments with *p*-chloro-*m*-cresol suggest that heating for 4 hours at 80° C., or for 15 minutes at 100° C., in presence of 1–400 *p*-chloro-*m*-cresol would suffice for sterilisation; this reagent is more effective in acid solution; at *p*H 5, 2 hours' heating at 80° C. are sufficient for sterilisation. The results of the various experiments are set out in tabular form, and tentative outlines for the process of sterilisation of medicaments are given. A table showing the aerobic colony counts in nutrient agar upon spore-infected preparations after they had been heated at 100° C. for the periods stated, with and without the addition of germicidal agents, is given below. The + sign after a number signifies that it is an under-estimate, owing to spreading growths.

Preparation	Test 1		Test 2		Test 3	
	15 mins.	30 mins.	15 mins.	30 mins.	15 mins.	30 mins.
Physiological saline alone	66+	16+	98+	19	110+	25
Physiological saline with						
p-Chloro-*m*-cresol 1 in 1000	16	5	11	2	53	14
,, ,, 1 in 500	3	0	3	0	21	3
,, ,, 1 in 400	2	1	4	0	17	2
Hexyl-resorcinol 1 in 3000	4	1	7	1	—	—
Phenol 1 in 200	—	—	—	—	26	20
Phenol 1 in 100	—	—	—	—	17	8
Tricresol 1 in 300	—	—	—	—	22	19

The author has previously drawn attention to the high lethal efficiency at 80° C. of hexyl-resorcinol in oils (*Pharm. J.*, 1934, 133, 447). This substance is unstable in aqueous solution. D. R. W.

Isolation of Water Leptospirae in Pure Culture and their Biology. H. Sugimoto. (*Japanese J. Exper. Med.*, 1938, **16**, 143–159; *Bull. Hygiene*, 1939, **14**, 75.)—A new method for the isolation of water leptospirae is described. The number of leptospirae is first increased by cultivation in the following enrichment medium:—(1) A 20 per cent. suspension of faeces in tap water is boiled for one hour and then filtered. (2) A 3 per cent. suspension of agar in water is sterilised at 120° C. for twenty minutes and then run into test tubes in 7-ml. quantities without filtering. The water to be tested (83 ml.) is mixed with 10 ml. of the faeces filtrate (1) and 7 ml. of melted agar (2) and the resulting mixture is poured into four Petri dishes and cultivated for two weeks at 30° C. The presence of agar was found to increase the percentage of positives from 38 when faeces only was used to 77·4. The mixed culture is next grown in a chloral hydrate medium prepared by mixing a 10 per cent. solution of chloral hydrate with 0·5 per cent. agar in water in such proportions that the resulting mixtures contain 0·1, 0·07 and 0·05 per cent. of the former. These mixtures are transferred to tubes in 10-ml. quantities and, after seeding, the cultures are incubated at 25° C. for ten days. The tubes containing 0·1 per cent. of chloral hydrate gave the best results for primary mixed cultures. Pure cultures were obtained on a medium consisting of 2 per cent. of agar, 0·06 per cent. of chloral hydrate and 10 per cent. of inactivated rabbit serum; the colonies of leptospirae formed were surrounded by a white ring. In semi-solid agar media two rings are formed round the colonies. Water leptospirae have a haemolytic action on the erythrocytes of various animals including those of man, the horse, guinea-pig, rabbit and rat; they also reduce oxyhaemoglobin. The optimum conditions for the growth of pure cultures appear to be a temperature of 30° C., a serum-content of 20 per cent. and a *p*H of 7·4 to 7·6. These organisms are aerobic. D. R. W.

Agricultural

Determination of Organic Carbon in Soils. Modification of the Chromic Acid Reduction Method. E. R. Purvis and G. E. Higson, Jr. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 19–20.)—W. T. Degtjareff (*Soil Sci.*, 1930, **29**, 239) and L. E. Allison (*id.*, 1935, **40**, 311) have found that, although Schollenberger's chromic acid reduction method (*id.*, 1927, **24**, 65; 1931, **31**, 483) for the determination of organic carbon in soils does not give quantitative results as compared with the combustion method, the results are constant and reproducible, and the correct value may be obtained by the use of the factor 1·15. In the method 0·2 to 0·5 g. of soil is oxidised with a measured quantity of a standard solution of chromic acid in sulphuric acid, the extent of reduction of the reagent being determined by titration with 0·2 *N* ferrous ammonium sulphate solution, with diphenylamine as indicator. Various devices have been suggested for accelerating the oxidation reaction (*cf.* Degtjareff, *loc. cit.*, and Walkley and Black, *id.*, 1934, **37**, 29), but they are shown to impair the accuracy of the method. In particular, this is now proved to apply to Degtjareff's proposal (*loc. cit.*) that the mixture should be heated for 10 minutes at 165° C. in a bath of sulphuric acid, the titre of the chromic acid being reduced by 0·008 and 0·072 *N* when temperatures of 140° and 180° C. are used. This is due to both evaporation and reduction of the chromic acid in contact with the glass container, parts of which may attain a temperature of 800° C. over an open flame. The authors therefore suggest balancing the temperature and the period of heating, so as to render negligible the change in strength of the reagent. An electric oven suitable for this purpose is described; it accommodates 10 test-tubes (25 × 150 mm.) and is capable of operating at 400° C., and of raising the temperature of the 10 ml. of solution in each test-tube to 175° C. in about 3 minutes. If the top two-thirds of the test-tubes project out of the oven, and so act as a condenser, this and the fact that the actual glass does not attain a temperature over 400° C. minimise the loss in strength of the solution. Tests on 5 soils containing 0·65 to 5·22 per cent. of organic matter, showed that the results after oxidation for 3 minutes were the same as those obtained by heating over the open flame for 90 seconds; thus 100 samples may be oxidised in an hour. The reagent is best prepared by heating for 1 hour on the water-bath, with occasional stirring, a mixture of 10 g. of powdered potassium dichromate (which has previously been dried at 100° C. for 1 hour) and 500 ml. of a mixture of equal volumes of phosphoric acid and sulphuric acid. This produces

a reagent approximately 0·4 N in (oxidising) strength and of maximum stability; there is no necessity to add phosphoric acid subsequently to activate the diphenylamine indicator; the stated proportions of acids ensure the sharpest end-point.
J. G.

Colorimetric Determination of Traces of Nitrates in Form of Ammonia. H. Sallinger and Y. Hwang. (*Z. anal. Chem.*, 1939, **115**, 174–177.)—For the determination of ammonia in filtered soil solutions strongly discoloured by humic substances not removable by precipitation with ferric hydroxide, etc., the authors convert the nitrates into ammonia, which is distilled. Twenty ml. of the solution are diluted with 120 ml. of water in a conical 300-ml. flask. One g. of Devarda's alloy and 0·5 g. of magnesia are added, and 20 to 40 ml. are distilled into a small flask containing a few ml. of water. The distillate or an aliquot part is Nesslerised. Another portion of solution is distilled as before but without the alloy, and the ammonia thus found is subtracted from the first result. A blank determination must be made with each assay. The process is sensitive to 0·01 mg. of nitrogen, and quantities of 0·02 to 0·5 mg. can be accurately determined. W. R. S.

Organic

Determination of Small Amounts of Alcohol by means of Sulphuric Acid—Chromate Mixture. A. Rapin. (*Helv. Chim. Acta*, 1939, **22**, 72–75.)—When ethyl alcohol is oxidised by means of a mixture of potassium dichromate and sulphuric acid, variable quantities of acetaldehyde are formed, and this leads to erratic results. The trouble can be overcome by carrying out the oxidation in a pressure-flask. Exactly 1 ml. of *N* potassium dichromate solution, 1 ml. of 20 per cent. sulphuric acid and 1 ml. of the alcohol solution to be tested, are measured into a 50-ml. pressure-flask having a long neck fitted with a stopper kept in place by a wire clip. After being stoppered the flask is immersed in a boiling water-bath for 10 minutes. A blank experiment without alcohol is made at the same time. The two flasks are allowed to cool and the contents are carefully rinsed out and treated with a strong solution of potassium iodide, the liberated iodine being titrated with 0·1 *N* sodium thiosulphate solution. One ml. of *N* solution is equivalent to 0·0115 g. of ethyl alcohol. Almost exact agreement with the theoretical value was obtained by the method, which can also be used to estimate methyl alcohol. F. A. R.

***m*-Bromobenzazide as a Reagent for the Identification of Amines. P. P. T. Sah and L.-H. Chang.** (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 8–11.)—Organic azides decompose on heating in an anhydrous solvent to form gaseous nitrogen and an isocyanate; in the presence of an amine, the isocyanate reacts with it, giving an insoluble substituted urea, the properties of which can be used to characterise the amine. Secondary amines react with more difficulty than primary amines; amides, amino-acids, and amino-phenols also react, but the yield of the product is not as high as with primary amines. The following experimental procedure has been adopted.

Preparation of m-*Bromobenzazide.*—Ethyl *m*-bromobenzoate was condensed with hydrazine hydrate to form *m*-bromobenzhydrazide (*m-bromobenzoylhydrazine*), which separated from dilute ethyl alcohol in white needles, melting at 152° C. Ten g. of the *m*-bromobenzhydrazide were dissolved in 100 ml. of glacial acetic acid, and the solution was cooled. An ice-cold solution of sodium nitrite (10 g. in 20 ml. of water) was slowly dropped into the hydrazine solution, with continuous stirring and efficient cooling. The reaction mixture was stirred for 10 minutes and then diluted with 300 ml. of cold water, which precipitated the azide as a heavy yellowish oil. The product was extracted with three portions of toluene (50, 25, and 25 ml.), and the toluene layer was separated, washed with cold dilute sodium carbonate solution and then with water, and immediately dried over fused calcium chloride. After standing overnight the solution was filtered and stored in a flask containing fused calcium chloride. Ten ml. of the solution were found to contain about 1 g. of the azide.

Identification of Amines.—To 5 ml. of the azide solution in a large test-tube was added a clear solution of an equivalent weight of amine in dry toluene. The test-tube was fitted with a cork carrying a long glass tube to act as a condenser, and the mixture was heated in an oil-bath to 120° C. and kept at that temperature for at least 15 minutes. Some condensation products separated immediately from the hot solution, and others after standing and cooling. The crystals of the *m*-bromophenylureas were filtered off with suction, washed with toluene, and recrystallised from a suitable solvent (ethyl alcohol, benzene, acetone or a mixture of ethyl alcohol and benzene). Tables give the physical properties and the analyses of the *m*-bromophenylureas prepared from 23 amino compounds. The following are typical melting points of the *m*-bromophenylureas:—Aniline, 196–197° C.; *o*-toluidine, 212–213° C.; *m*-toluidine, 248–249° C.; *p*-toluidine, 222–223° C.; α-naphthylamine, 259–260° C.; β-naphthylamine, 240–241° C.; diphenylamine, 141–142° C.; acetamide, 201–202° C.; acetanilide, 118–119° C. E. M. P.

p-Bromobenzazide as a Reagent for the Identification of Alcohols. P. P. T. Sah and K.-Y. Tao. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 12–16.)—Azides of organic acids react with alcohols to give crystalline urethanes, the properties of which can be used to characterise the alcohol. Primary alcohols give the best results; with secondary and tertiary alcohols either the yield of urethane is poor or no reaction occurs. The following experimental procedure has been adopted.

Preparation of p-*Bromobenzazide.*—*p*-Toluidine was converted into *p*-bromotoluene by the Sandmeyer–Gattermann reaction (Bigelow, *Organic Syntheses*, 1925, V, p. 21), and the purified product was oxidised with potassium permanganate to *p*-bromobenzoic acid (Adams and Marvel, *Organic Chemical Reagents*, University of Illinois Bulletin, 1921, III, 31), which was esterified to ethyl *p*-bromobenzoate (Errera, *Gazz. Chim. Ital.*, 1887, **17**, 211). Condensation of the ester with hydrazine hydrate gave *p*-bromobenzhydrazide (Curtius and Portner, *J. prakt. Chem.*, [2], 1898, **58**, 201; Kahl, *Chem. Zentr.*, 1904, II, 1493; Kendall and Sherman, *J. Am. Chem. Soc.*, 1908, **30**, 1451; Wang, Kao, and Sah, *Science Reports, National Tsing Hua University*, 1935, A III, 279–284). From 10 g. of the hydrazide, dissolved in 80 ml. of glacial acetic acid, after treatment in the cold with 10 g. of sodium nitrite in 25 ml. of water, a 90 per cent. yield of *p*-bromobenzazide (Sah, Kao, and Wang, *J. Chinese Chem. Soc.*, 1936, 4, 193–197) was obtained. The product was filtered off, washed thoroughly in cold water, sucked dry, and finally dried in a vacuum desiccator over phosphorus pentoxide; it must be absolutely dry before being condensed with the alcohols.

Identification of Alcohols as p-*Bromophenylurethanes.*—0·5 g. of the reagent is treated, in a test-tube previously dried by heat, with the calculated quantity of the alcohol dissolved in petroleum spirit (ligroin, b.p. 90–120° C.), and the mixture is heated under reflux in an oil-bath first at 80° C. and finally at 120° C. for half-an-hour. The boiling solution is filtered hot and the residue is washed once with boiling ligroin. With alcohols the urethanes of which have to be recrystallised from dilute alcohol (ethylene glycol, glycerol, and borneol), benzene solutions of the reactants are used. After the solution has been heated under reflux at 80° C. for half-an-hour, the solution is evaporated to dryness and the residue is extracted with dilute alcohol. Usually the urethanes crystallise out quickly, but standing overnight in an ice-box gives better results. Tables give the physical properties and the analyses of the *p*-bromophenylurethanes from 27 alcohols. E. M. P.

Fats and Fatty Acids with an Odd Number of Carbon Atoms. W. Keil, H. Appel and G. Berger. (*Z. physiol. Chem.*, 1939, **257**, I–III.)—The chain length of coconut oil fatty acids was increased by one carbon atom by means of the series of transformations: fatty acid → alcohol → bromide → nitrile → fatty acid. Certain properties of the glyceride of the product, which contained an odd number of carbon atoms, were compared with those of the natural coconut oil. The two glycerides, when administered to rats, reduced the respiratory quotient to the same degree, were hydrolysed at the same rate by pancreas lipase, gave rise to body fats that had identical iodine values in rats receiving them in their diets, and when fed in large quantities to goats resulted in the excretion of urine having the same carbon : nitrogen ratio. F. A. R.

Oxidation Products of the Unsaturated Acids of Linseed Oil. L. C. A. Nunn and I. Smedley-Maclean. (*Biochem. J.*, 1938, **32**, 1974–1981.)—The oxidation of the mixed acids of linseed oil by means of cold alkaline potassium permanganate solution was studied. A 96 per cent. yield of dihydroxystearic acid was obtained from the oleic acid present and the quantitative nature of the oxidation was unaffected by the proportions of linolic or linolenic acids. The method can therefore be employed to estimate oleic acid. The yields of tetrahydroxy-acids from the linolic acid present was only 28 to 32 per cent., whereas yields of 52 to 54 per cent. were obtained from the pure acid. The yields of hexahydroxy-acids from the linolenic acid were 40 to 52 per cent., but only 22 to 25 per cent. from the pure acid. Thus in mixtures linolenic acid is more readily degraded than linolic acid and exercises a protective action on the oxidation of the latter. An acid, $C_{12}H_{18}O_4$, was isolated from the oxidation mixture and identified as the γ-lactone of hydroxy-Δ1 : 2-decene-1 : 10-dicarboxylic acid; this was also identified as a product of the oxidation of pure linolic acid. The γ-lactone of 3: 4-dihydroxydecane-dicarboxylic acid was also identified together with a small amount (1·2 per cent.) of azelaic acid. F. A. R.

Some Aquatic Animal Oils. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, **1938**, **41**, **320B–321B**.)—*Eel-liver Oil.*—Successive extractions of eel livers with alcohol and ether yielded approximately 8 per cent. of oil. After removal of the acetone-insoluble substances (approximately 4 per cent. of the extract) a brownish-yellow oil, semi-solid (*i.e.* liquid containing crystals) at 12° C. was obtained. It had the following constants:—d_4^{15}, 0·9318; n_D^{20}, 1·4810; acid value, 68·1; saponification value, 181·6; iodine value, 184·4; unsaponifiable matter, 5·50 per cent. The unsaponifiable matter was deep orange-yellow and crystalline. It melted for the most part above 100° C. and contained 71·8 per cent. of sterol and a small amount of methanol-insoluble substance (probably hydrocarbon). The oil yielded brownish-orange-yellow crystalline fatty acids having m.p. 33–34° C., neutralisation value 191·5, iodine value 192·6, and yielding 65·5 per cent. of ether-insoluble bromides.

Eel-bone Oil.—This was a yellow liquid with a little solid deposit. It gave d_4^{15}, 0·9247; n_D^{20}, 1·4755; acid value, 3·6; saponification value, 194·0; iodine value, 129·7; unsaponifiable matter, 0·87 per cent. In the antimony trichloride test it gave a faint blue colour. The unsaponifiable matter was orange-yellow and crystalline, partly melting at 100° C. The fatty acids were orange-yellow and crystalline and gave m.p., 35–36° C.; neutralisation value, 201·6; iodine value, 133·9; yield of ether-insoluble bromides, 27·4 per cent.

Carp-liver Oil.—This was an orange-yellow liquid, depositing solid matter at 12° C. It gave d_4^{15}, 0·9288; n_D^{20}, 1·4795; acid value, 0·82; saponification value, 192·6; iodine value, 169·7; unsaponifiable matter, 0·59 per cent. The unsaponifiable matter was orange-yellow and crystalline and melted above 100° C. The fatty acids were orange-yellow and crystalline, and gave m.p., 30–31° C.; neutralisation value, 198·6; iodine value, 176·7; yield of ether-soluble bromides, 47·9 per cent.

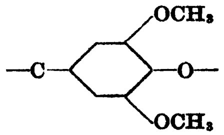
Dolphin-liver Oil.—Part of the liver of a dolphin, treated in the same way as eel-liver, yielded 4·7 per cent. of crude oil, containing 29 per cent. of acetone-insoluble substances. The refined (acetone-soluble) portion was a brownish red-yellow liquid. The oil gave the following constants:—d_4^{20}, 0·9171; n_D^{20}, 1·4784; acid value, 59·7; saponification value, 154·6; iodine value, 163·3; unsaponifiable matter, 18·91 per cent. The unsaponifiable matter was yellow-orange and crystalline, with m.p. usually above 100° C., iodine value 147·0 and sterol 70·2 per cent. The fatty acids were dirty yellowish-orange and crystalline, and gave m.p., 35–36° C.; neutralisation value, 191·8; iodine value, 169·7; yield of ether-insoluble bromides, 56·1 per cent.

The crude extract from the rest of the liver (2616 g.) was saponified and the unsaponifiable matter was extracted with ether; yield, 19 g. This contained approximately 2 g. of methanol-insoluble matter. After removal of vitamin A (by filtration of a petroleum spirit solution through a column of Japanese acid clay) and of sterol (by means of digitonin) and subsequent treatment in ether with animal charcoal, about 1 g. of an orange-yellow, very viscous liquid hydrocarbon, insoluble in acetic anhydride, was obtained. Its constants and properties were: d_4^{25}, 0·9084; n_D^{20}, 1·5134; iodine value, 330·1; molecular weight (cryoscopic method), 1089; carbon 85·65 per cent., hydrogen 11·93 per cent. The additive bromine compound (containing 66·97 per cent. of bromine), was a white ether-insoluble powder sintering and blackening at 165–170° C. The hydrochloride (recrystallised from acetone) was a nearly white powder, sintering at about 116° C. and melting (with decomposition) at 125–127° C. (chlorine 31·23 per cent.). The cause of the high molecular weight of the hydrocarbon, which is nearly double that of the hydrocarbon of the liver oils of certain whales, etc., which resemble it in other constants and properties, is unknown. Polymerisation of the original hydrocarbon by the acid earth is suggested, but the other constants appear to contradict this. When squalene was similarly filtered through the earth the molecular weight and carbon and hydrogen contents were not altered but the other constants were considerably changed. E. B. D.

Wool Wax. T. Kuwata and M. Katuno. (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 227–229B). *Two New Alcohols.*—The unsaponifiable matter of merino wool wax was dissolved in five times its weight of methanol and separated into fractions according to solubilities. Fraction 4 was dissolved in acetone, the solution was cooled to −10° C., and the soluble semi-solid reddish-brown material (23 per cent. of the total unsaponifiable matter) was acetylated and distilled under reduced pressure. The first two fractions, distilling at 120–190° C. and 190–210° C., were repeatedly re-distilled, and the fraction obtained between 210–225° C. (10 mm. mercury) with saponification value 178, was collected. The free alcohol from this fraction, separating as a bulky mass from organic solvents, was converted into phenylurethane and recrystallised from petroleum spirit, the crystals finally obtained melting at 79·5 to 80·0° C. Lano-octadecyl alcohol of m.p. 42–43° C. was then obtained from the urethane by reaction with sodium ethylate, and its composition agreed with the formula $C_{18}H_{38}O$. The original fraction (6), amounting to about 6 per cent. of the total unsaponifiable matter, soluble in methanol at −10° C., was converted into its acetyl ester and distilled under reduced pressure. The fraction of highest b.p. was a yellow liquid with saponification value 156. The free alcohol of this fraction, when recrystallised from acetone, petroleum spirit or ethyl acetate, was a white crystalline powder with m.p. 78–78·5° C.; its composition agreed with the formula $C_{21}H_{40}(OH)_2$, and it was termed lanyl alcohol. After it had been dried for a month in a vacuum desiccator its m.p. rose to 79·5–80·0° C. Lanyl alcohol does not absorb bromine at room temperature and gives a phenyl urethane with m.p. 97·97° C. *Isolation of Cholesterol from Wool Wax.*—The unsaponifiable matter of wool wax is extracted with hot methanol, in which isocholesterol is only sparingly soluble, and the crude cholesterol is precipitated by cooling the solution to room temperature. Acyclic alcohols separate first as a gelatinous precipitate, followed by cholesterol in fine long needles. When recrystallised once from alcohol or methyl acetate these yield crystals of pure cholesterol with m.p. 145–146° C. The acetyl ester has m.p. 113–114° C.

D. G. H.

Chlorine-Sodium Sulphite Colour Reaction of Woody Tissues. II. Bearing of the Colour Reaction on the Constitution of Hardwood Lignin. W. G. Campbell, J. C. McGowan and S. A. Bryant. (*Biochem. J.*, **1938, 32,** 2138–2141.)—The well-known colour reaction given by woody tissues with sodium sulphite following chlorination is not characteristic of lignin only, but is also given by tannins. It was concluded from this that the reaction was probably specific for phenolic compounds containing the 1 : 2 : 3-trihydroxybenzene nucleus, though this was not known to occur in native lignin until recently; but it is now established (Harris, D'Ianni and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 1467) beyond doubt that lignin is aromatic in structure. In the present work various phenols and phenolic derivatives were exposed to gaseous chlorine and then treated with sodium sulphite, and of these, gallic acid, trimethylgallic acid and syringic acid gave colours similar to that given by lignin; 1 : 2 : 3-trimethoxy-benzene gave only a faint reaction, but this may have been due to the insolubility of the compound in water. Gallic acid and syringic acid also gave the colour on treatment with other oxidising agents in presence of sodium sulphite, but trimethylgallic acid gave the colour only after preliminary chlorination, and this was found to be due to partial demethylation by the chlorine, the resulting hydroxy-compound being responsible for the colour reaction. Since, so far as is known, chlorination must also be applied to hardwood lignin before the characteristic colour is produced by sodium sulphite, there exists a close analogy between the behaviours of lignin and trimethylgallic acid, and it is suggested that lignin contains the modified pyrogallol nucleus



as a recurring unit. F. A. R.

Action of Ethanolamine on Woody Tissue. L. E. Wise, F. C. Peterson and W. M. Harlow. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 18–19.)—W. G. Van Beckum and G. J. Ritter (*Paper Trade J., Tech. Sect.*, 1937, **104**, 19, 49) have described a method for the determination of holocellulose, which gives almost the whole of the total carbohydrate fraction of the cell-wall, as well as part of the methoxyl compounds and most of the acetyl compounds present in the wood. It depends on alternate treatment with chlorine and a 3 per cent. solution of monoethanolamine in 95 per cent. alcohol, and the following modified method described by the present authors is based on this work:—The sample (*e.g.* 1 g. of oven-dried, beech heart-wood sawdust) was extracted for 5 hours in an oil-bath at approximately 170° C. with 50 ml. of monoethanolamine, the solvent in contact with the wood being just below the boiling-point. An Erlenmeyer flask fitted with a funnel covered with a watch-glass was found to be suitable; cork or rubber stoppers must be avoided. The mixture was then diluted to 50 ml. with water, and the residue was separated and washed on a sintered glass crucible and then bleached for 20 minutes in the crucible, which was placed in a covered beaker in saturated chlorine water. The liquid was removed by suction and replaced by sulphurous acid which, after 3 minutes, was itself removed, and the residue was washed. Treatment in succession with a hot 3 per cent. solution of sodium sulphite for 30 minutes, chlorine water, water, sulphurous acid, water and dilute ammonia then followed, and the residue was finally dried and weighed. The two results for the wood in question were 60·4 and 60·5, the average Cross and Bevan cellulose value of the sample being 60·7 (per cent. ?). If this concordance between the two methods is confirmed for other woods, the ethanolamine method offers the simpler and more convenient procedure. Harlow and Wise (*Amer. J. Botany*, **1938**, **25**, 217) obtained results of 30·0 and 29·4 per cent. for the evaluation of the woody portions of rhizomes of brake fern by a similar ethanolamine method and by the Cross and Bevan method, respectively. Blocks of the dry sapwoods of red pine, sitka spruce, red elder and catalpa, which had been aspirated under cold water and stored in 15 per cent. alcohol, were cut into transverse sections (10μ thick), immersed in cold mono-ethanolamine, and examined, at intervals, after washing in water and treatment of separate portions with the phloroglucinol reagent for lignin and with 72 per cent. sulphuric acid. After 3 days the phloroglucinol produced an orange-red colour, and the acid showed no signs of disintegration of the walls. After 2 weeks the former reaction was negative, and there were indications of partial disintegration in acid (especially with the conifers), whilst after 3·5 months disintegration of the secondary walls was almost complete. In every instance the "compound middle lamella" of Kerr and Bailey remained, showing that the reagent was unable to attack the lignin of the central layers. Further experiments with a wider range of woods at 28° C. and with boiling ethanolamine gave similar results, the rate of delignification being greater as the temperature rose. The middle lamella was attacked and removed almost completely after 2 to 6 hours in the boiling solvent. The fact that the appearance of the section resembles closely that obtained as the result of chlorination or bromination followed by the action of dilute sodium sulphite or 10 per cent. ammonium hydroxide solution, adds support to the opinion that ethanolamine cellulose and Cross and Bevan cellulose are very similar, if not identical. J. G.

Inorganic

Indicator for Saturation, Oxidation, and Precipitation Methods. E. Schulek and P. Rózsa. (*Z. anal. Chem.*, 1939, **115**, 185–195.)—*p*-Ethoxychrysoidin hydrochloride, $C_2H_5O{\cdot}C_5H_4{\cdot}N_2{\cdot}C_6H_3(NH_2)_2{\cdot}HCl$, is blackish-red, and soluble in water or alcohol to produce a deep red colour which turns yellow in the interval *p*H 3·5 to 5·5, thus being intermediate between methyl red and methyl orange. A drop of a 0·2 per cent. solution in water or 96 per cent. alcohol is used in saturation analysis, the end-point being sharp and easily observed. Methyl orange must be used for the cold titration of carbonates and bicarbonates, but the new indicator is more suitable for borates; when 0·1 *N* solutions are used the removal of carbon dioxide by boiling is not essential, but with 0·02 or 0·01 *N* solutions this should be done before the end-point is reached. The aqueous 0·2 per cent. solution is a reversible indicator for oxidimetric work, the red tint being discharged by a drop of 0·1 *N* ceric sulphate or potassium permanganate solution, and restored by a trace of sodium hyposulphite, and on slight warming by a ferrous salt, arsenite, or antimonite. In an acidified bromide solution, a drop of 0·01 *N* bromate deepens the red tint, but a second drop discharges it. The indicator was successfully applied in the titration of ferrous salt solutions with 0·1 and 0·01 *N* ceric sulphate and 0·01 *N* permanganate solutions. The iron solutions were acidified with 10 ml. of 50 per cent. sulphuric acid and 5 ml. of 20 per cent. phosphoric acid, and diluted to 50 or 100 ml. Arsenite and antimonite solutions were titrated with 0·1 and 0·01 *N* bromate solutions after addition of 1 g. of potassium bromide, 5 ml. of strong sulphuric acid, and for antimony, 0·5 to 1 g. of tartaric acid. The indicator acts in 5 per cent. hydrochloric acid solutions, but a higher acidity is prejudicial to its sensitiveness, hence the solution must be suitably diluted. Neutral 0·1 and 0·01 *N* iodide and 0·1 *N* thiocyanate solutions may be titrated with silver nitrate in presence of 0·5 ml. of a 0·02 per cent. alcoholic solution of the indicator. The originally yellow tint changes to rose-red upon addition of silver solution; the tint gradually deepens, but changes at the end-point to pale lemon-yellow with flocculation of the silver precipitate in the manner of adsorption indicators. A small correction is required for silver solution consumed by the indicator. W. R. S.

Quinaldinic Acid as an Analytical Reagent. P. Rây and N. K. Dutt. (*Z. anal. Chem.*, 1939, **115**, 265–268; *cf.* ANALYST, 1934, **59**, 199; 1935, **60**, 494.)—Zinc can be determined as quinaldinate in presence of silver, mercuric or cuprous salts after addition of thiourea, which forms stable complex cations with these metals. The neutral solution is treated with 8 g. of potassium iodide, which converts mercury into the complex iodide and precipitates silver iodide. A freshly-prepared solution of 4 to 8 g. of sodium bisulphite and a solution of 4 to 8 g. of thiourea are added, copper being reduced to cuprous salt and silver iodide dissolving. The solution is acidified with 2 to 5 ml. of dilute acetic acid, diluted to 200 ml., heated on the water-bath, stirred, and treated drop by drop with excess of a neutral 5 per cent. solution of sodium quinaldinate. The precipitate is left to settle, collected in a Gooch crucible, and washed with hot water—first by decantation—until free from precipitant. The crucible is dried at 125° C. and weighed. Zinc factor, 0·1529. W. R. S.

Colorimetric Determination of Small Quantities of Iron Oxide in Glass and Glass-making Sand. R. C. Chirnside. (*J. Soc. Glass Tech.*, 1938, **22**, 41–44.)—The thioglycollic acid method has been applied to glass. The method is unaffected by most of the basic or acid radicals which interfere with the thiocyanate test. A 0·2-g. sample is treated in a platinum crucible with 15 ml. of hydrofluoric acid and 2 ml. of dilute sulphuric acid (1: 6), and the acids are evaporated to dryness. The residue is strongly ignited for 15 minutes and fused with 2 g. of sodium carbonate, the mass is dissolved in 10 ml. of hydrochloric acid and the solution is diluted to 100 ml. Twenty ml. are transferred to a 50-ml. Nessler tube and 10 ml. of 10 per cent. tartaric acid solution, 1 ml. of thioglycollic acid and 10 ml. of dilute (1: 1) ammonia are added. The purplish-red colour produced is matched by introducing into another Nessler tube, containing similar amounts of reagents, a standard iron solution (1 ml. = 0·00001 g. of Fe_2O_3). Lovibond colour-glasses are available for the iron-thioglycollic acid determination. A blank test on the reagents is advised. Owing to the readiness with which platinum apparatus in general use becomes contaminated with iron a platinum crucible should preferably be reserved solely for this determination. S. G. C.

Determination of Thallium by means of Thiourea. C. Mahr and H. Ohle. (*Z. anal. Chem.*, 1939, **115**, 254–257.)—The solution containing 2 per cent. of free perchloric acid is treated with an equal volume of 10 per cent. thiourea, which precipitates $TlClO_4{\cdot}4CS(NH_2)_2$. The beaker is cooled for half-an-hour in running water, and the precipitate is collected in a porous glass crucible and washed with cold 5 per cent. thiourea solution slightly acidified with perchloric acid. The precipitate is dissolved in hot water and, if lead is present, the aqueous solution is again acidified with perchloric acid and the precipitation is repeated. Thallium is recovered as chromate, the solution of the purified precipitate being treated with 5 ml. of 10 per cent. ammonia and enough potassium chromate to yield a 2 per cent. solution. After standing for 12 hours the precipitate is collected in a porous porcelain crucible and washed with 1 per cent. potassium chromate solution followed by 50 per cent. alcohol until the washings are colourless. The precipitate is dried at 120° C. and weighed. W. R. S.

Detection of Carbon Disulphide. A. Castiglioni. (*Z. anal. Chem.*, 1939, **115**, 257–259.)—On adding 2 or 3 drops of a 2 per cent. solution of piperazine in 95 per cent. alcohol to 1 ml. of the solution to be tested, a yellowish-white precipitate is formed if carbon disulphide is present. The reaction is given by solutions in various solvents, *viz.* benzene, toluene, xylene, acetone, deca- or tetra-hydronaphthalene. Neither hydrogen sulphide nor thiophene reacts with piperazine under these conditions. The reaction will detect 0·0005 g. of carbon disulphide, this quantity giving a cloudiness after some minutes' standing.

W. R. S.

Colour Reaction for Sulphur. L. Van Itallie. (*Pharm. Weekblad*, 1938, **75**, 1445–1448.)—The author's reaction (ANALYST, 1938, **63**, 624) is best carried out by shaking the substance to be tested with 1 to 2 ml. of 4 *N* sodium hydroxide solution, and then adding carefully 1 to 2 ml. of pyridine. If the liquids are mixed in such a way that the subsequent formation of separate layers is not affected, 4 zones are eventually apparent, *viz.* the lowest (sodium hydroxide) layer, which is colourless, a yellow zone at the interface between this and the pyridine, and a green and a blue zone in the pyridine layer. If the blue zone is not apparent, the green zone being present, dilution with pyridine is recommended. The minimum quantity of sulphur detectable is 5μ, but the blue colour fades fairly rapidly and eventually disappears, and this is attributed to the formation of a sulphur compound of different composition. The green zone is due to admixture of the colour of the adjacent (yellow) zone. With homeopathic triturates, 50 mg. of sample should be shaken with 1 ml. of pyridine, and on the addition of 2 drops of the 4 *N* alkali, the blue colour appears if sulphur is present. Positive results are obtained with both precipitated sulphur and colloidal sulphur in a highly-dispersed state. The reaction is unaffected by the presence of chloroform, ether or benzene, but carbon disulphide prevents the formation or, if added subsequently, destroys the blue colour. The mechanism of the reaction is discussed. Thus, J. C. Gil (*Z. anal. Chem.*, 1894, **33**, 54) showed that when a weak solution of an alkaline polysulphide (but not a monosulphide) was added to a flask containing warm 96 per cent. alcohol (the air having been previously displaced by the alcohol vapour) a faint sky-blue colour was obtained which subsequently turned green, or which, on cooling the flask in air, disappeared, leaving a turbidity due to the formation of sodium thiosulphate. The blue colour did not return on warming again, and selenium and tellurium gave negative results. Paternòen and Mazucchelli (*Atti R. Accad. dei Lincei*, 1907, **16**, 1, 465) showed that acetone may be used in place of alcohol, and that a high temperature is essential. The function of the organic solvent was believed to be the limitation of the degree of ionisation of the substance produced by the reaction, and this appeared to be confirmed by the stabler colours obtained when pyridine or ethylamine was used, and the absence of a blue colour in a medium containing only water. Van Itallie found that powdered metallic selenium dissolves in the mixture of pyridine and alkali to give a yellow-brown solution, which on dilution with pyridine deposits red selenium. The reaction is favoured by heating, and under these conditions alcohol may replace pyridine. When acetone was used a red solution was obtained which had a narrow and a wide absorption band in the yellow-green and blue-green regions, respectively. In this connection Espil (*Bull. Soc. Chim.*, 1910, **7**, 155) has shown that the action of alkali on selenium is to produce a selenide, which deposits red selenium on exposure to air. When metallic tellurium is warmed with alcohol and solid potassium hydroxide, a red-violet colour is produced, and on dilution with water a fine dark grey powder separates. J. G.

Microchemical

Identification of very small Quantities of Copper and Mercury by means of Urobilin. C. A. Sagastume and V. Oliva. (*Revista de Ciencias Quim. la Plata*, 1938, **12**, 43–45.)—The method is based on the reaction of urobilin with salts of copper or mercury to form complexes which give pink colours in dilute solution and purple colours in stronger solutions. The reaction has already been applied to the micro-determination of copper (Emmerie, *Chem. Weekblad*, 1930, **27**, 552; Abst., ANALYST, 1930, **55**, 718). The present authors used the following method for mercury. To 0·5 ml. of a dilute aqueous solution of a mercury salt is added 0·15 ml. of a 1/10,000 alcoholic solution of urobilin; in a control tube 0·5 ml. of water is treated with the urobilin solution. A pink colour develops but is obscured by a yellow tint. The pink complex is extracted by introducing 0·1 ml. of chloroform into the tube, and allowing it to stand; the pink colour can then be detected in the chloroform layer. In absence of copper this reaction can be used to detect 0·001 mg. of mercury, which can be identified in solutions as dilute as 1 in 10,000. E. M. P.

Micro-Colorimetric Determination of Aluminium in Plant Ash. O. Schams. (*Mikrochem.*,* 1938, **25** 16–46.)—A number of different colorimetric methods for the determination of aluminium were tested, a Leitz colorimeter and a Lange photo-electric colorimeter being used. Methods tried included those using

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*Now united with *Mikrochimica Acta*.

as reagent (1) haematoxylin, (2) the ammonium salt of aurintricarboxylic acid, otherwise known as aluminon or aurin; (3) 1-2-5-8-oxyanthraquinone or quinalizarine, (4) the ammonium salt of nitroso-phenylhydroxylamine or cupferron, (5) alizarine S, (6) eriochromcyanin R conc. G, (7) morin, (8) precipitation with 8-hydroxyquinoline followed by colorimetric determination of the oxine with Folin's reagent, (9) colorimetric determination of the oxine by coupling with sulphanilic acid, (10) colorimetric determination of the oxine by coupling with naphthionic acid. The last-named method is recommended as the most suitable for amounts of aluminium from 10–50γ in plant ash. *Method.*—The hydrochloric acid solution of the ash is evaporated to 3 or 4 ml. in a centrifuge tube. Iron and aluminium are separated as phosphate from the other constituents by the addition of at least 20 mg. of iron as ferric chloride, 0·5 ml. of saturated ammonium phosphate solution and 0·5 ml. of saturated ammonium chloride solution; the mixture is rendered just alkaline to phenolphthalein with dilute ammonia. The tubes are heated for 2 minutes in a glycerin bath and then cooled, 3 ml. of glacial acetic acid are added and the mixture is diluted with water to 8 ml., stirred for 3 minutes and centrifuged for 10 minutes at 2000 r.p.m. The precipitate is washed with 8 ml. of 10 per cent. acetic acid and, after removal of supernatant liquid, is dissolved in 2 ml. of water and 1 to 2 drops of hydrochloric acid, and reprecipitated with 0·25 ml. of saturated ammonium phosphate solution and 0·25 ml. of saturated ammonium chloride solution. The rest of the procedure is the same as before except that 1 ml., instead of 3 ml. of glacial acetic acid is added before centrifuging and the precipitate is washed finally with water only, and dissolved in 0·5 to 2 ml. of 10 per cent. hydrochloric acid. To separate the aluminium from the iron, the ferric iron is converted into ferrocyanide ion by means of 6 to 15 drops of freshly-prepared, saturated solution of potassium cyanide to which has been added 0·2 ml. of saturated ammonium tartrate solution and 3 to 8 drops of conc. ammonia. After 2 minutes' heating the reduction is completed with 1 drop of saturated potassium metabisulphite solution. The liquid is then treated with 0·5 ml. of saturated ammonium chloride solution and heated to 60° C., and the aluminium is precipitated by means of 2 to 8 drops of oxine solution (prepared according to Berg). The volume of the solution should be so adjusted that 10γ of aluminium are precipitated from 0·5 to 1 ml. and 20 to 50γ from 2 ml. The precipitate is left for 30 minutes at 60° C. and for 4 hours at 30° C. It is then washed either with 3 ml. of cold water, in 3 portions and with benzene, or with hot 50 per cent. ammonium chloride solution. For filtration, a B 2 porcelain filter-crucible is used, with suction. Finally the precipitate is dissolved (if less than 50γ by means of warm 30 per cent. acetic acid, but larger quantities by means of 10 drops of glacial acid or 3 drops of conc. hydrochloric acid) and transferred with the aid of suction to a 200-ml. measuring cylinder; warm water is used for washing. Coupling and diazotisation are carried out by the addition of 1 ml. of 0·345 per cent. sodium nitrite solution and 1 ml. of naphthionic acid solution (1·17 g. in 100 ml. of 0·01 *N*-sodium hydroxide solution) to 150 ml. of the liquid. After 2 minutes, 20 ml. of 8 *N*-sodium hydroxide solution are added and the liquid is made up to the mark with water. The resulting permanganate-coloured solution may be compared with the colour obtained with a standard oxine solution (1 ml. $\equiv$ 4γ Al) either at once or after an hour (kept in dark). For values ranging from 10γ to 40γ the error does not exceed 2 per cent. The method was tested exhaustively on artificial salt mixtures and on plant ash to which known amounts of aluminium had been added. Fifty references are given.

J. W. M.

Apparatus for Micro Steam Distillation. J. Erdös and B. Lárzló. (*Mikrochim. Acta*, 1938, 3, 304–305.)—The apparatus may be constructed in two forms (Fig. 1 and Fig. 2), the second for the distillation of substances that volatilise with difficulty. The flask A is filled with water, through C to such a height that the bottom of B is submerged. A few pieces of pumice are added to prevent bumping. The substance to be distilled is placed in the bottom of the tube B, either by means of a capillary pipette, if liquid, or by forceps, if solid. The stopper F, with attached delivery tube K, is then filled. For very volatile substances K is fitted with a water-condenser. When the water boils in A the steam passes into B through the narrow tube *b*. J. W. M.

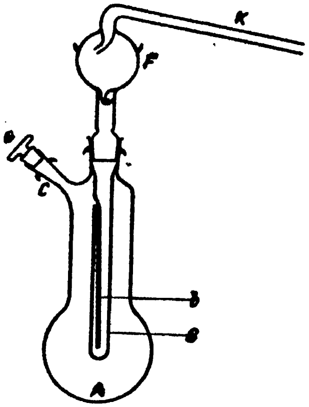

Fig. 1

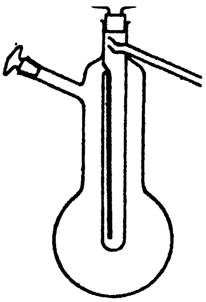

Fig. 2

References to Current Microchemical Literature. (*Mikrochem.*, 1938, 25, 349–382.)—References are given with complete titles and, where necessary, a further explanation of contents, not exceeding 1 line. In each instance the address of the author's laboratory is included. The references are arranged in alphabetical order of the authors' names under the following headings:—Inorganic: preparative and analytical, 53 references; physico-chemical and physical methods, 42 references; organic: preparative and analytical, 84 references; biochemical, 100 references; medico-chemical methods, 37 references; pharmacology, toxicology and forensic chemistry, 20 references; plant chemistry, agricultural chemistry and food chemistry, 36 references; applied chemistry (technical, mineralogical, etc.), 10 references; apparatus, 27 references. J. W. M.

Collected References. Micro-Halogen Determinations: Fluorine and Chlorine. F. Hernler and R. Pfeningberger. (*Mikrochem.*, 1938, 25, 267–348.)—References are given with brief descriptions of the methods as follows:—

Fluorine (*qualitative*), 54 references; (*quantitative*) (*a*) gas-volumetric, 3 references; (*b*) gravimetric, direct, when precipitation with lanthanum acetate or as the triphenyl tin fluoride are most recommended, 10 references; indirect, by precipitation as calcium fluoride and volatilisation in various ways, 7 references; (*c*) etching methods, 3 references; (*d*) volumetric, 18 references; (*e*) colorimetric and potentiometric, 36 references; (*f*) nephelometric, 1 reference; (*g*) spectrographic, 3 references. *Chlorine* (*qualitative*), 36 references; (*quantitative*) (*a*) gas-volumetric, not recommended; (*b*) volumetric, especially applied to drinking water, 8 references; (*c*) colorimetric, 42 references. *Chloride ion* (*quantitative*) (*a*) gravimetric, 10 references; (*b*) volumetric, 33 references; (*c*) determination in biological material, especially in blood and urine, 120 references. *Chlorine* in organic liquids, 10 references. *Chloride*, colorimetric and nephelometric, 22 references; spectrographic, 1 reference; *Chlorine*: determination of the element in organic compounds, 8 references. The total number of references cited exceeds 400. J. W. M.

Physical Methods, Apparatus, etc.

Viscometer for the Routine Determination of Proteolytic Activity of Malts. J. R. Koch, O. Nelson and L. Ehrnst. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 35–41.)—The viscometer consists of two Erlenmeyer flasks, the top one inverted and connected in a vertical position at the neck with the lower one by means of a capillary tube, which enables the solution under examination to flow from one to the other. An air-tube, passing through the two stoppers, is provided, so that no air-pressure will be built up in either flask when the viscometer is inverted for subsequent determinations to be made. In one of the two forms illustrated the necks are fitted with rubber stoppers through which pass the capillary viscosity tube (bore 1·5 mm., length 2·5 to 3·7 cm.), and the open air-vent tube, which terminates about half-way down each flask. The ends of the capillary tube should project beyond the rubber stoppers, so that the solution may run freely from them without touching the sides of the flask; allowance for this should be made when measuring out the 50 ml. of solution used for the determination (see below). In the other (all-glass) type, the capillary tube is sealed into the closed necks of the flask, the air-vent (which is also used for filling and emptying the apparatus) being a T-tube, each arm of which is bent at the end and sealed into the respective flask near the base. At room temperature 50 ml. of water should pass through the capillary in 35 to 36 seconds. A fresh solution of a pure gelatin is prepared by stirring 25 g. into 125 ml. of water, allowing the vessel to stand for 30 minutes, and then placing it in a water-bath at 60° to 65° C.; the solution is diluted to 250 ml. in a graduated flask. The malt is ground in a Miag-Seck mill, and 20 g. are mixed with 100 ml. of water at 40° C. and maintained at 40° C. for 30 minutes. The mixture is filtered, and 35 to 40 ml. of filtrate are placed in a water-bath at 40° C. for 8 minutes, 25 ml. being then mixed with 50 ml. of the gelatin solution at 40° C., and the time noted ("zero-time"). The viscometer is warmed to 40° C., and viscosity determinations are made on the same 50 ml. of the mixture at intervals of 15 minutes for 3 hours, by repeatedly inverting the apparatus, an extra predetermined volume being used if the capillary tube projects into the flask (see above). Typical curves are given for various malts, to illustrate the effects of differences in processing. It is convenient to indicate the proteolytic strength in terms of the number of minutes required to produce a fall in viscosity of 20 per cent. The choice of this time is justified by the shape of the curves shown, because (especially with papain and trypsin, see below), the curves may fall sharply at first and flatten out to a horizontal line almost parallel with the time-axis as the quantity of enzyme is increased. If the curves are extrapolated back to the time-axis (the "zero-time"), the time of flow is the same as that obtained in a blank experiment with a mixture of gelatin and an infusion of malt which has been boiled to destroy the enzymes. It is therefore unnecessary to standardise the instrument when it is used in this way, and purchasers of malts are enabled to arrange any number of samples in order of their proteolytic activities. Viscometers prepared with equal lengths of capillary tubing cut from the same piece give the same proteolytic strengths for the same malt. Curves are also given for the evaluation of the activities of trypsin and papain, and reliable results were obtained with 6 to 500 and 50 to 1500 parts of enzyme per million of substrate, respectively. The effect of the *p*H at which the determination is made is also considered, and it is concluded that 5 to 6 is a suitable range, the variation in activity between these values being within the order of experimental error. Moreover, the *p*H varied very little during the run, showing that the gelatin is adequately buffered, so that the addition of buffer salts (which might interfere with the reaction) is avoided. If it is desired to compare results obtained in different laboratories, the respective viscometers must be standardised with two liquids, *e.g.* water and a 40 per cent. solution of sucrose, which are used to determine the constants A and B in the formula for the kinematic viscosity (U/V), *viz.* ($AT-B/T$). U is the absolute viscosity in centipoises, V the density of the liquid in g. per ml., and T the time of flow in seconds. A calibration-curve is thus constructed by plotting U/V against T; values of U/V for water and the sucrose solution at 40° C. are 0·662 and 2·94, respectively. Universal values for the proteolytic activity of malts (P) may then be obtained from the expression ($250-t$), where t is the time in seconds to produce a fall of 20 per cent. in the value of U/V; each minute of this time corresponds with a difference of 1 unit in P. The theoretical justification for the expression of activities in this way is discussed, and analyses of malts, which include values of P, are tabulated. J. G.

Determination of Density Differences by the Flotation Temperature Method. M. Randall and B. Longtin. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 44–46.)—The method, which is based on the work of Richards and his co-workers (*J. Amer. Chem. Soc.*, 1912, **34**, 599; 1914, **36**, 1; and 1916, **38**, 1000) and of Briscoe and his co-workers (*J. Chem. Soc.*, 1934, 1207), depends on the variation in density of a liquid with temperature and the dependence on this of the behaviour of a float in the liquid. An apparatus is described which enables the flotation temperature of 0·1 ml. of sample to be determined to within 0·005° C., and its applications in connection with the separation of the isotopic forms of water are outlined. The sample was purified by distillation, first over alkaline permanganate solution and then (if ammonia was present) from phosphoric acid, carbon dioxide and other dissolved gases being removed by heating it, with agitation, at 50° C. in a vacuum. It was then placed in a small Pyrex tube containing a float and immersed in a thermostatically-controlled water-bath, the temperature of which was alternately raised and lowered (by addition of hotter or colder water, respectively) until the temperature limits above which the float sank and below which it rose were brought to within 0·005° C. as shown by a Beckmann thermometer. The movement of the float was followed by observing, through a telescope provided with a cross-hair, the extent to which it intercepted a beam of light. It was found necessary to agitate both the float in the tube and the mercury column of the Beckmann thermometer to prevent sticking, and this was conveniently achieved by means of an electric buzzer placed in contact with the respective supports. The micro-floats were made from the thin-walled glass tubing obtained by drawing out the central part of a Pyrex test-tube, this tube being sealed at one end, whilst the other was drawn out to a fine long capillary about 4 mm. away from the sealed end. The float was adjusted to ride in the liquid in question by cutting off pieces of the open end of the capillary until a mark on the capillary was on a level with the surface of the liquid. The end of the capillary was then melted gradually until the volume of the float was so decreased that it would just barely sink. Adjustments in the other direction were made by heating the float until the glass just softened, when the internal expansion of the air produced the necessary increase in volume. The drop of glass at the end of the capillary served to weight the float, so that it could ride in the tube in an upright position without sticking. Floats about the size of a grain of wheat may be made in this way, and the diameter of the sample tube in which they are immersed must be adjusted so as to be the smallest in which the float will move freely; the smaller the clearance, however, the longer the time required (usually 10 to 15 minutes) for the float to react to changes in density. The flotation temperature is then given by the point of intersection of the curves representing temperature plotted against the density of the sample and that of the float; at this temperature the float and sample have the same density. Richards (*loc. cit.*) has shown that if the flotation temperatures of the float in 2 standard liquids (whose densities are known over a wide range of temperature) are determined, the coefficient of expansion of the glass may be calculated and allowance made for the variation in the density of the float at different temperatures. It is thence shown how the density of a sample may be calculated from its flotation temperature and from that of a substance of known density. Application to the calculation of densities and compositions (*e.g.* of heavy water) are discussed, consideration being given to the thermal expansion of the float, changes in the temperature of flotation of the reference sample, and deviations from the laws of ideal solutions. A slide rule or nomogram for calculating the percentage composition (*e.g.* of heavy water) from the flotation temperature is described.

J. G.

Calculation of the Area Basis Metal Exposed at Discontinuities in the Tin Coating of Tinplate. W. E. Hoare. (*Phil. Mag.*, **1938**, **26**, 1077–1084; *International Tin Research Dev. Council, Publication No.* 86.)—The calculation is based on the experimentally determined results of the effect of thickness of the tin coating on porosity, and on theoretical work on the size of non-reactive areas on the steel surface necessary to produce normal pores. The area of basis metal exposed, A, is found to decrease regularly with increase of thickness of coating and is given by the expression $A = 1{\cdot}1 \left\{ \frac{Y}{Y^{1{\cdot}785}} - 0{\cdot}119 \right\}$ sq. mm. per sq. metre, where Y is the thickness of coating expressed in pounds per basis box. Selected results are as follows:

A	1	0·5	0·25	0·1
Y	1	2	4	7

S. G. C.

Reviews

Library Guide for the Chemist. By Byron A. Soule. Pp. xiii + 302. New York: McGraw-Hill Book Co., Inc.; London: McGraw-Hill Publishing Co., Ltd. 1938. Price 15s. net.

This book is intended to provide training in the use of bibliographical tools, especially those peculiar to the field of chemistry.

The first two chapters deal with the arrangement of a library and catalogue from the aspect of the reader rather than of the professional librarian. Sources of biographies are next referred to in detail. The succeeding sections refer to periodicals and the evaluation of original papers and the use of summaries appearing in abstract journals, reviews, reports and encyclopaedias. Then follow sections devoted to specialised reference books including textbooks and tables of constants. These sections are divided into the four major divisions of chemistry—inorganic, organic, analytical and physical. Remaining sections relate to patents and patent literature, and Government publications, and finally there is an informative section on the presentation of oral and written reports.

Primarily the book is intended as a guide to the use of keys and summaries, and in this respect it is excellent. In particular the explanation of the arrangement and instructions as to the use of extensive compilations and summaries such as "Beilstein" and the "International Critical Tables" should be of considerable value to students.

It is regrettable, however, that the book is marred by errors in historical facts. On page 53 the impression is given that The Chemical Society did not publish an abstract section until 1862, thirteen years after the French, whereas 82 pages of foreign abstracts appeared in the very first volume of the Quarterly Journal published in 1848. The first French abstracts were included not in the "Bulletin," at that time a publication of 84 pages, but in two substantial volumes entitled "Répertoire de Chimie pure (et appliquée)." The forerunner of the "Zeitschrift für angewandte Chemie" was entitled "Zeitschrift für die chemische Industrie," and not "Zentralblatt für technische Chemie."

In numerous instances the bibliographical information is out of date, but limitation of space only permits mention of a few examples. The 1924 edition of "Sutton" is stated to be "the standard English text"; the revised edition of 1935 is not mentioned. Britton's "Hydrogen Ions," 1929, is referred to, but not the edition published in 1932, whilst Findlay's "Phase Rule," 1923, is quoted, but not that of 1931.

The index has at least three wrong alphabetical sequences and seven errors which may be attributed to the printer.

Notwithstanding these blemishes the book is a useful one, though it cannot be so strongly recommended as it would have been if these defects were not present.

F. W. CLIFFORD

STANDARD METHODS FOR TESTING TAR AND ITS PRODUCTS. Standardisation of Tar Products Tests Committee. Second Edition. Pp. xiii + 434. London: S.T.P.T.C., 166, Piccadilly, W.1. 1938. Price 21s. net.

It is generally recognised that standard tests cannot be rigidly permanent but need periodic revision in order to keep pace with new developments both in manufacturing processes and analytical technique, and also to meet the changing requirements of users of the basic materials and their products. Accordingly, during the nine years that have elapsed since the issue of the First Edition of this publication, the Tar Products Tests Committee has been engaged in collating the experience of users of the 1929 tests and, with the assistance of a Revisionary Panel and eight Panel Groups, has now published a second edition which renders the first edition both inadequate and obsolete.

The general lay-out of the new edition follows closely that of the first. Despite a saving of space achieved, without loss of clarity, by cutting down the size of many of the diagrams, the new volume has grown from 296 to 434 pages. Certain tests which experience has shown were not in general demand have been omitted, many have been modified or replaced by others of greater accuracy, while a large number of additional tests called for by increasing stringency of modern requirements have been introduced. By way of examples, Section I on General Principles provides for the determination of density as well as specific gravity both by the bottle and hydrometer methods. The Committee also recommends that, as an indication of the presence of low-boiling constituents, the "drip" point be replaced by the temperature reading when 5 per cent. of the sample has distilled. Under Refined Tar is included a description of the method recently published by the Committee for the determination of the Equi-viscous Temperature. Lower Boiling Fractions are now dealt with under Crude Benzole, Light and Middle Oils and Refined Lower Boiling Products. The Section on Coal Tar Phenols—the term preferred to Tar Acids as tending to dispel the idea that tar products contain corrosive acids—includes methods for the determination of phenol in phenol-cresols mixtures and of phenol and the cresol isomers in cresylic acid, together with a facsimile reproduction of the U.S. Customs distillation method for cresylic acid. The extended field of use for creosote oil is reflected by the inclusion of tests for fluidity, calorific value, flash-point, viscosity and coke residue. It is noted that Gooch crucibles prepared with asbestos have been substituted for sintered glass crucibles, which have proved unsatisfactory for filtration of matter insoluble in toluole. Softening-point methods for pitch have been supplemented by inclusion of the Ring and Ball and the Half-Inch Cube tests. British Standard Apparatus has been adopted so far as possible, and in such cases only summaries of the relevant British Standard Specifications are given in the Apparatus schedules composing Appendix I. In Appendix II is to be found a very useful table showing the physical constants of the more common constituents of coal tar. Graphs have now been included, more conveniently, in the text instead of at the end of the book, but copies printed on special paper suitable for mounting are still obtainable from the office of the Committee.

The high standard of printing and material used in the first edition is maintained in the present volume. The price, however, has increased nearly threefold, and it can only be assumed that the first edition was published at an uneconomic figure. The Committee is to be congratulated on the excellence of the second edition of Standard Tests, and there is no doubt that it will be universally welcomed by all who are concerned in the production, marketing and use of coal tar and its products.

F. R. ENNOS

THE PHYSICAL PROPERTIES OF COLLOIDAL SOLUTIONS. By E. F. BURTON, B.A., Ph.D. Third Edition, prepared with the assistance of MAY ANNETTS SMITH, M.A., Ph.D. Pp. viii + 235. London: Longmans, Green & Co. 1938. Price 15s.

The first edition of this well-known work appeared in 1916, and the second in 1921. Very considerable research has been published during the ensuing 17 years, but the volume under review has only been increased by some 45 pages.

The Preface by Professor Burton states that over one-half has been completely re-written. "Our aim has been to accentuate the contribution of the study of colloidal solutions to the confirmation of the basic principles of the kinetic theory of matter. For example, more prominence has been given to the treatment of the Brownian movement and its immediate consequences and less to the abstruse optical properties of suspensions than in former editions. One cannot hope to treat fully all phases of the large field, but we have aimed at some degree of completeness in those phases which have been selected for treatment." This admission prepares the student for the very specialised character of the volume and for the absence of much which he would normally expect to find.

The thirteen chapters deal successively with:—Colloidal Solutions Defined; Historical Background; Classification and Preparation of Colloidal Solutions; Forces Regulating the Size of Colloidal Particles; The Ultramicroscope; The Brownian Movement; The Distribution of Particles in a Colloidal Solution—Macroscopic Equilibrium and Microscopic Fluctuations; Determination of Avogadro's Number; The Optical Properties of Colloidal Solutions; The Size of Colloidal Particles; Electrokinetic Phenomena; The Coagulation of Colloidal Solutions; Conclusion.

To the reviewer this book is a real disappointment. It is agreed that the earlier editions, especially the first, filled a gap in the text-book literature on colloids. To-day, however, the subject is so extended that Burton's treatment is quite inadequate. The references to original sources are too few. Again, even admitting the specialised treatment in limited fields of inquiry, there is inadequate account of the more modern work. The chapter dealing with electrokinetic phenomena may be cited. Herein is given an excellent account of early work and a detailed discussion of the Helmholtz Double Layer and the related formulae for electro-endosmosis. Modern views on the structure of the double layer are ignored, and the names of Gouy, Stern, Lens and others well known in this connection do not appear. Other chapters have similar deficiencies as regards modern investigations.

The book can be read with profit as a statement of the classical aspect of colloid chemistry. In this respect the chapters dealing with the ultramicroscope and with the Brownian movement deserve special mention.

The reviewer would assess this volume as a sound introduction to the study of colloidal systems, typical of the earlier schools, but to be read with the understanding that modern developments must be studied in larger works or special monographs. The book is well bound and printed and reasonably priced.

WILLIAM CLAYTON

MODERN ASPECTS OF INORGANIC CHEMISTRY. By H. J. EMELÉUS, D.Sc., A.R.C.S., and J. S. ANDERSON, Ph.D., A.R.C.S. "Twentieth Century Chemistry" Series, edited by J. C. PHILIP, F.R.S. Pp. xi + 536. London: George Routledge & Sons, Ltd. 1938. Price 25s.

Where inorganic chemistry is concerned much water has flowed under the bridges since the opening of this century, and it is amazing to realise how much of the foundations of chemistry has been dug up without seriously dislocating the enormous superstructure which had been raised thereupon. Dislocation of textbooks is, however, inevitable; hence the many attempts to produce books that will fill in the gaps that have appeared. To this category belongs the book under review, although it is one which is strongly individual and is difficult to classify at all. The preface states that "this volume has been designed to give a review of some of the important developments which have taken place in Inorganic Chemistry during the last two decades or so, and to relate those developments to the science as a whole"; this may be taken as a very fair account also of what the book has achieved. The form adopted is that of a series of more or less disconnected essays, each dealing very thoroughly with some field of modern research and giving, in the authors' words, "a cross-section of the subject" as ordinarily presented. There are fifteen such essays headed as follows:—Atomic Structure and the Periodic System; Atomic Weights and Isotopes; Structure of Molecules of Inorganic Compounds; Co-ordination Compounds and Inorganic Stereochemistry; Poly-acids and Silicates; Hydrogen and the Hydrides; Free Radicals of Short Life; Non-metallic Oxides and Related Substances; Recent Chemistry of the Non-metals; Peroxides and Per-acids; Recent Chemistry of the Metals; Metallic Carbonyls, Nitrosyls and Related Compounds; Intermetallic and Interstitial Compounds; Reactions in Liquid Ammonia and Liquid Sulphur Dioxide; Radio-activity and Atomic Disintegration. The various essays are well, concisely and clearly written; this does not, however, imply that they are easy reading; the time is probably yet distant when all these modern theories shall be welded into one clearly comprehensible system, and this book is addressed to "teachers, honours students and research workers." To get a similar amount of information on some of this modern work one would need to have recourse to a text-book very large and very recent indeed, and, apart from the labour of extracting that information from thence, it is very doubtful if any existing text-book contains more than a fraction of it.

Two minor criticisms that may be advanced refer not so much to this book in particular as to certain tendencies which are becoming wide-spread and are in need of regulation. One of these tendencies is the more or less arbitrary assignation of symbols to organic radicles; a specially glaring example of this occurs on p. 142, where the symbol allotted to propyl is indistinguishable, in type or otherwise, from that accepted for praseodymium. The other criticism refers to a matter in which the authors, presumably, had no choice, the fault lying with the original investigators; the use of the word "co-ordination" both in a chemical and a crystallographic sense does not tend towards the ready comprehension of an argument in which it is being used in both senses.

There is a certain resemblance in plan between this book and Morgan and Burstall's *Inorganic Chemistry*: *A Survey of Modern Developments* (*cf.* ANALYST, 1937, **62**, 422), but the two books differ widely in content and treatment and there is no serious competition between them.

The volume is attractively bound and the printing is excellent. Proof reading, too, seems to have been well carried out, for only one slip has been noted (p. 449), unless the statement (p. 489) that the number of helium atoms produced by 1 g. of radium in a year ($4{\cdot}53 \times 10^{18}$) is "in good agreement" with the number of α particles emitted ($4{\cdot}53 \times 10^{18}$) is another slip and not merely a rather quaint mode of expression. An index of 8 pages (less than twice the length of the list of contents) seems very inadequate in a book of this type.

A significant sentence occurs in the preface—"If this practice (their method of reference) has led to an apparent preponderance of references to foreign—especially German—investigations, this must be taken as reflecting the comparative neglect of Inorganic Chemistry in Britain to-day." A glance at many recent indexes of the *Journal of the Chemical Society* will amply confirm this statement. The authors' "main objective" of "presenting the subject as one which still ranks as an absorbing experimental science and which offers unlimited opportunities for the development of new experimental methods and the exploration of little known fields" has been fully achieved, and the book is warmly to be recommended to all who wish to keep in touch with the more recent work on the subject.

B. S. EVANS

QUALITATIVE INORGANIC ANALYSIS. By A. J. BERRY, M.A. Pp. 147. Cambridge:
University Press. 1938. Price 6s.

While much in the traditional system of qualitative chemical analysis is likely to remain of value for some time to come, rapid progress has been made in recent years with new developments—new reagents, spot tests and so on. The author has evidently given careful thought to the difficulties thus created in the presentation of the subject to students, for he has very ably selected from the old and the new to give in a book of modest size, and, consequently, of moderate price, a balanced treatment well suited to modern needs.

The book is in two subdivisions: General (28 pp.) and Special (remainder). The first gives a brief non-mathematical account of relevant chemical theories followed by a description of methods and reagents. The second gives reactions of the metals (49 pp.), reactions of the acid radicals (36 pp.), systematic analyses for metals (12 pp.) and examination for acid radicals (11 pp.). It will thus be seen that most of the space is devoted to reactions, a good knowledge of which is of the first importance to the student. A number of elements formerly classified as "rare," *e.g.* vanadium and molybdenum, are included. There are one or two pages on dry tests; these are too useful on occasion to merit complete exclusion. Among the newer reagents described are ammonium mercurithiocyanate (for cobalt, cadmium and zinc), diphenylcarbazide (the value of this reagent in testing for traces of chromic acid is not well emphasised), salicylaldoxime (for copper) and quinalizarine (for magnesium and beryllium). The value of zinc uranyl acetate as a means of testing for sodium, however, is not mentioned. The group separations are clearly described and a tabular summary of these is given at the end of the book.

The style throughout is clear and concise. The author states that the book was written primarily for his own pupils. It deserves to be widely adopted for teaching purposes.

S. G. CLARKE

MIKROMETHODIK. QUANTITATIVE BESTIMMUNG DER HARN-, BLUT- UND ORGANBESTANDTEILE IN KLEINEN MENGEN FÜR KLINISCHE UND EXPERIMENTELLE ZWECKE. By LUDWIG PINCUSSEN. Sixth Edition. Pp. vii + 193, 31 illustrations. Leipzig and Vienna: Franz Deuticke. 1937. Price RM.5.

The fifth edition of this laboratory handbook was published seven years ago, and having regard to the recent developments of micro methods applied to biology, a new edition was required to bring it up to date. New matter includes the determination of carbon in urine, the sulphur of glutathione, indican in blood and a procedure for the determination of the fractions of blood protein. A new method is substituted for the method previously given for the determination of sodium in blood. The methods described are mainly nephelometric, volumetric and colorimetric rather than gravimetric. There is also a chapter on gas analysis.

As the book has been brought up to date in many respects, it is a pity that it is still incomplete. Among the descriptions of burettes, the 10-ml. Pregl burette with automatic filling is not mentioned, the modern Parnas and Wagner Kjeldahl method for nitrogen is not described, nor yet the use of selenium as a catalyst, or even of perhydrol to accelerate the decomposition of organic matter. No methods are given for the determination of silica in urine or blood, of arsenic and lead in urine or of alcohol in blood. The book retains its original format, and is of a very convenient size for laboratory reference. The index, as in so many German publications, is very incomplete.

J. W. MATTHEWS

APRIL, 1939 Vol. 64, No. 757

8-5-39

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Institute of Chemistry, Russell Square, W.C.1, at 5 p.m., on Friday, March 3rd, the President, Professor W. H. Roberts, in the chair.

Certificates were read in favour of the following candidates for Membership:—H. A. Frediani, Ph.D., B.A., M.S., and B. S. Platt, Ph.D., M.B., Ch.B.

The following were elected members of the Society:—F. C. Collins; R. Crosbie-Oates, B.Sc., F.I.C.; Professor H. E. Fierz-David; J. G. Fife, M.Sc., F.I.C.; W. C. Hughes; N. E. G. N. Iyengar; W. E. Kemp; H. C. Lockwood, B.Sc., F.I.C.; W. Marsden; F. Michel; A. H. Rheinlander, M.Sc., F.I.C.; L. W. Ruddle; J. Straub; R. G. Thin, B.Sc., F.I.C.; H. Wilkinson, B.Sc., Ph.D.; E. G. Williams, M.A., A.I.C.; F. R. Williams, Ph.D., B.Sc., A.I.C.

The Annual General Meeting of the Society then followed. The Honorary Treasurer, Dr. E. B. Hughes, presented the accounts for the year, and the Honorary Secretary, Mr. L. Eynon, presented the Report of the Council.

The following were elected as Officers and Council for the year 1939–40:

President.—Professor W. H. Roberts, M.Sc., F.I.C.

Past Presidents serving on the Council.—F. W. F. Arnaud, Bernard Dyer, John Evans, Edward Hinks, G. Roche Lynch, G. Rudd Thompson.

Vice-Presidents.—E. B. Anderson, J. R. Nicholls, W. H. Simmons, T. P. Hilditch (*Chairman, North of England Section*), T. Cockburn (*Chairman, Scottish Section*).

Hon. Treasurer.—E. B. Hughes.

Hon. Secretary.—Lewis Eynon.

Other Members of Council.—E. A. M. Bradford, R. C. Chirnside, D. C. Garratt, G. Van B. Gilmour, L. H. Lampitt, G. W. Monier-Williams, H. E. Monk, A. Scholes, W. M. Seaber, F. G. H. Tate, G. Taylor, E. Voelcker, J. B. McKean (*Hon. Secretary, Scottish Section; ex officio*), J. R. Stubbs (*Hon. Secretary, North of England Section; ex officio*).

Following the Annual General Meeting a lecture was delivered by Sir Henry Dale, C.B.E., M.D., F.R.S., on "Biological Standardisation."

The lecture will be published in THE ANALYST.

Obituary

ARTHUR SMITHELLS

ARTHUR SMITHELLS was born at Bury, Lancashire, on May 24th, 1860. The son of James Smithells, a railway manager, he was educated at the University of Glasgow; next, under Roscoe and Schorlemmer, at Owens College, Manchester, where he held a Dalton Scholarship; then, after graduating B.Sc. in the University of London, he took supplemental courses at Munich and, with Bunsen, at Heidelberg. In 1883 he was appointed assistant lecturer at Owens College, and two years later succeeded Professor T. E. (later Sir Edward) Thorpe as Professor of Chemistry in Yorkshire College, Leeds, which, in 1887, became a constituent college of the Federal Victoria University, Manchester, and in 1904 was incorporated as the University of Leeds. Having co-operated actively in all the affairs of the University, and for many years held the position of Pro-Vice-Chancellor, he retired from the Chair with the title of Emeritus Professor in 1923. Throughout his academic career he was a notable protagonist for the applications of science in the very widest sense to be given a prominent share in the science teaching in the universities. He insisted upon the part that the universities should play in the life of the community; the several departments of applied chemistry inaugurated in Leeds during the tenure of his Chair there, and the success which those departments achieved, were in no small measure due to his forceful advocacy of their incorporation in the organisation of his university. He received the degree of D.Sc. *honoris causa* from both Leeds and Manchester, and, in 1926, a Research Scholarship in his honour was founded in the former University.

He was a successful and popular teacher, having a clear and incisive delivery and remarkable experimental skill. No one realised more clearly than he did the increasing burden laid upon the students consequent upon the progress of the science. He steadily developed his department throughout his tenure of the Chair, and many of his students distinguished themselves in their subsequent careers.

From 1896 to 1899 he was Chairman of Convocation of Victoria University; in 1907, at Leicester, he was President of Section B at the seventy-seventh meeting of the British Association for the Advancement of Science, when he gave a masterly address on the subject of flame, ignition temperatures and the mechanism of luminosity, followed by a brief review of the state of chemical science at that time.

In the same year he became Honorary Educational Adviser on Home Science and Household Economics to King's College, London. In 1911 he was President of the Society of British Gas Industries, in which capacity he emphasised the importance of scientific research and exerted his influence with the industry to establish the Livesey Professorship in Coal, Gas, and Fuel Industries, in the University of Leeds. In 1912 he became a member of the Teachers' Registration Council; in 1913 and 1914 he was special lecturer in the University of the Punjab; in 1915 he was visiting lecturer in anti-gas training in the Northern Command, and from 1916 to 1919 held the rank of Lieutenant-Colonel—Chief Chemical Adviser (Anti-gas Training), G.H.Q., Home Forces—receiving, in 1918, the honour of C.M.G. in recognition of his services.

From 1923 to 1937 he was Director of the Salters' Institute of Industrial Chemistry, in which office he was mainly responsible for the selection of graduates who were provided with grants to continue their preparation for chemical industry —a post in which he was thoroughly happy.

His contributions to science related mainly to flame and spectrum analysis. He was also the author of papers, reports and addresses on educational subjects. A selection of his addresses was published in a book entitled *From a Modern University*, published by the Oxford University Press.

He was elected a Fellow of the Royal Society in 1901, and served on the Council from 1912 to 1913 and 1915 to 1917—the latter period including one year as Vice-President. He served on the Council of the Chemical Society from 1896 to 1900, was a Vice-President for three periods, 1905–1908, 1917–1920, and 1927–1930, and in 1935 was Harrison Lecturer. He was elected a Fellow of the Institute of Chemistry in 1887; he served as a Member of the Council for the periods 1890–1893, 1896–1899, and 1905–1908; as Vice-President from 1915–1917 and 1923–1926; as President, from 1927—the year in which the Institute celebrated the Jubilee of its foundation—to 1930; again as a Vice-President from 1930–1933, and as a Censor from 1927–1935.

He was elected an Honorary Member of this Society in 1927.

My first recollection of Professor Smithells goes back to May, 1892. A figure of distinguished bearing, he at once commanded my interest. He was speaking at a conference which had been called to consider the Regulations for the admission of Fellows and Associates to the Institute of Chemistry, and referred particularly to the difficulty of deciding which technical colleges and institutions should be recognised for the training of candidates for the Associateship. A previous speaker had stressed the importance of the academic attainments of the teachers, and it was perhaps characteristic of Professor Smithells that he remarked that, for his own part, he would as soon see the merits of the institutions adjudicated upon by the physical weight of the teachers as by their academic degrees!

Possessing great charm of manner and a happy fluency, his speeches at public functions were usually buoyant, encouraging and not without humour. At Council and Committee meetings he had generally something to say on any matter of interest outside the ordinary routine business, although, out of consideration for the feelings of others, he was at times perhaps too diffident in criticism. A kindly good man all through, and devoted to doing good, he was beloved by many friends, and honoured by his colleagues in the profession.

He died at Highgate on February 8th, 1939, in his 79th year.

RICHARD B. PILCHER

ARTHUR WILLIAM KNAPP

Arthur William Knapp died at the General Hospital, Birmingham, on Friday, January 6th, 1939, after an operation which followed a short illness. Born in Handsworth, Birmingham, in July, 1880, he was educated at King Edward's Grammar School, Aston, and at Mason's College, later the University of Birmingham. He graduated B.Sc. (London and Birmingham) in 1901, and M.Sc. (Birmingham) in 1928. He passed the Examination for the Associateship of the Institute of Chemistry in 1903, proceeding to the Fellowship in 1906. After a year spent as chief assistant to Mr. J. Kear Colwell, Public Analyst for Holborn, and three years in Belfast as chief assistant to Mr. R. Barklie, the Public Analyst of that city, he returned to Birmingham, where in the laboratory of the City Analyst, Mr. J. F. Liverseege, he was a colleague of Mr. H. S. Shrewsbury and, for a short time, of Dr. G. D. Elsdon. Then for a few months he was a research chemist in the laboratory of Lever Bros. at Port Sunlight, and in the autumn of 1911 he came back to Birmingham as the first research chemist to Cadbury Bros., Ltd., Bournville. At the end of 1923 he was appointed chief chemist.

Elected a Member of this Society in 1911, he was a Member of the Council in 1916. He had served, too, on the Councils of the Institute of Chemistry, of the Society of Chemical Industry, and of the British Association of Chemists, and had also been Chairman of the Birmingham Sections of these three bodies and of the Midland Chemists' Committee. His death removes a figure of international reputation from the cocoa and chocolate industry. Whilst he had carried out much research work of importance to the food industry as a whole, his knowledge of the problems of the cultivation and fermentation of cacao had made him an authority whose views on these subjects were sought by growers and manufacturers throughout the world, and gained for him, in 1935, the *Médaille de Mérite de l'Office International du Cacao et du Chocolat*. His book, entitled *Cacao Fermentation*, published in 1937, is the standard work on the subject. He was for many years a contributor to the scientific and technical press, and many papers of which he was either sole or part author have been published in the pages of The Analyst.

The growing knowledge of the importance of vitamins led Knapp to enquire into the vitamin D potency of chocolate products, and in 1928 he and Coward announced the fact that cacao nib had a vitamin D content of 1 International Unit per gram. This was followed in 1934 by the publication of research showing that cacao shell had a vitamin D potency of at least one-quarter that of cod-liver oil, and this led to further research into the fuller utilisation of this product in the feeding of cattle, with a view to the vitamin D enrichment of the milk and butter yielded.

He was a brilliant chemist and an inspiring chief of the chemical staff at Bournville. He was devoted to his profession and spared nothing in its service, being particularly active in support of all movements towards unification of the profession and the security of its less fortunate members.

Knapp was also a man of wide general interests. He was a member of the Fabian Society, and in his early days in Belfast had preached socialism to the dock labourers there—often at considerable personal risk. He was widely read, was an able writer on many different subjects, a dramatist, an excellent amateur actor and dramatic producer, a clever artist and caricaturist. Of all men he was the most reserved as regards the mainspring of his own inner life and thought. He hated the sham and the false, which often aroused in him a caustic irony, but his gentle tolerance where he differed from the sincerely held views of others was a matter of envy to those of a hotter temperament.

His family life seemed to be ideal; there as elsewhere he was wise, courteous and loyal. The loss to his wife and family must be deep indeed, and we can but offer to them our sincere and respectful sympathy. J. R. JOHNSON

HARRY SILVESTER

HARRY SILVESTER died at Malvern on December 11th, 1938, in his 74th year.

He was a student for three years at Mason's College, Birmingham, under the late Professor (afterwards Sir William) Tilden. Later, at the University of Birmingham, he continued his studies under Professor Percy Frankland, and graduated B.Sc.

Meanwhile he obtained the Associateship of the Institute of Chemistry in 1887, and proceeded to the Fellowship in 1891; he served on the Council for two periods, 1917 to 1920 and 1923 to 1926. He joined our Society in 1892, and was a Member of Council in 1913 to 1914.

On leaving Mason's College, Silvester became an assistant in the laboratory of the Brymbo Iron & Steel Co., and a few years later was appointed chemist to Messrs. J. & S. Roberts, West Bromwich. About the year 1896 he established a consulting practice in Birmingham; he was mainly engaged there in metallurgical work, chiefly relating to the chemistry of iron and steel; he retired shortly before his death.

In 1894 he was appointed Public Analyst for the County Borough of West Bromwich and in 1902 Public Analyst for the County Borough of Dudley, and in 1904 he became consulting chemist to the then Oldbury District Council. He was also Gas Examiner for West Bromwich. He was a very active member of the Society of Chemical Industry, particularly of the Birmingham Section, which had his constant support. In 1899–1900 he was President of the Staffordshire Iron & Steel Institute. His reputation in the Black Country stood high.

And what of the man? Tall, well-built and of athletic tastes, he distinguished himself in games and sports; cricket, football, hockey and golf he played for many years, and played them all with more than average skill.

He was widely read, especially in scientific literature, and kept himself well up to date in all that related to analytical chemistry and in particular the chemistry of iron and steel.

Silvester and the writer were old schoolfellows, and the friendship begun in those days became closer with the passage of years and continued in intimacy to the end. He was a very genial, humorous and attractive companion and will be much missed by all who knew him.

JOHN WHITE

Annual Report of Council

MARCH, 1939

THE Roll of the Society numbers 857, an increase of 26 over the membership of last year.

The Council regrets to have to record the death of the following members:

E. R. Bolton
J. T. Dunn
H. D. Elkington
G. N. Huntly
P. H. Kirkaldy
A. W. Knapp
C. H. LaWall
H. Silvester
A. Smithells
F. W. Toms
A. Whitby

Bolton, who died at the age of 60, had been a member of the Society since 1905. He served the Society as Honorary Secretary for ten years and was subsequently elected President (1926–27), an office which he filled with high distinction. He continued to serve on the Council as a Past President until his death, and his loss both to the Council and to the Society will be deeply mourned.

Dunn, who died in his 81st year, had been a member of the Society for 33 years, and took a very active and distinguished part in its work. He was successively an Ordinary Member of the Council, Vice-President, and in 1930–31 President. As Past President he continued his service to the Council and the Society until his death. His loss is mourned by many members of the Society who knew him, and especially by members of the North of England Section (Obituary, ANALYST, 1939, 64, 155).

Elkington, who died at the early age of 48, had been a member of the Society for 27 years. After a short experience of academic work he joined a firm of patent agents, and subsequently started practice as a chartered patent agent which he continued until his death (Obituary, ANALYST, 1938, 63, 865).

Huntly, who died at the age of 72, had been a member of the Society since 1909. He was in practice as a consulting chemist and analyst and held appointments as Gas Examiner under a number of authorities. He served as Member of Council for two periods and was Vice-President in 1919–20 (Obituary, ANALYST, 1938, 63, 775).

Kirkaldy, who died in his 68th year, had been a member of the Society for over 30 years and served as a Member of Council in 1917–18. He began his professional career as demonstrator at King's College, and was subsequently appointed Assistant Professor. He gave long and ungrudging services to the Institute of Chemistry as Member of Council and Hon. Treasurer (Obituary, ANALYST, 1938, 63, 863).

Knapp, who died at the age of 58, joined the Society in 1911 and served on the Council in 1916. For many years he was Chief Chemist to Messrs. Cadbury Bros., and was an authority on cocoa and cocoa products (Obituary, ANALYST, 1939, 64, 246).

LaWall, who died at the age of 67, was elected a member of the Society in 1911. He was engaged in practice as consulting chemist and analyst and had been for 37 years on the staff and ultimately Dean of Pharmacy in the Philadelphia College of Pharmacy and Science. He made many contributions to pharmaceutical chemistry and for many years served on the Revision Committee of the U.S. Pharmacopoeia.

Silvester, who died at the age of 73, had been a member of the Society for 46 years. He was engaged in practice as a consulting and analytical chemist and was Public Analyst for Dudley, and he was well known as an authority on water analysis. He served on the Council of the Society in 1913–14 (Obituary, ANALYST, 1939, **64**, 247).

Smithells, an Honorary Member of the Society, died at the age of 78. He had had a very distinguished academic career and was for many years Professor of Chemistry at Leeds University. He was President of the Institute of Chemistry from 1927–30 (Obituary, ANALYST, 1939, **64**, 244).

Toms, who died at the age of 82, had been a member of the Society for 54 years. He was for 47 years Official Analyst to the States of Jersey and made many investigations on soils and fertilisers with special reference to conditions in Jersey (Obituary, ANALYST, 1938, **63**, 695).

Whitby, who died at the age of 71, was elected a member of the Society in 1910. He was engaged in practice as consulting and analytical chemist and metallurgist in Johannesburg.

During the year seven Ordinary Meetings of the Society have been held and the following papers have been communicated:

"Hair Dyes. I. The Chemistry and Analysis of Henna." By H. E. Cox, D.Sc., Ph.D., F.I.C.

"Microchemical Investigations on Siliceous Dusts." By Janet W. Matthews, Ph.D., F.I.C.

"The Gravimetric Estimation of Germanium." By G. R. Davies, B.Sc., Ph.D., and Sir Gilbert Morgan, D.Sc., LL.D., F.R.S.

"Analysis of Vinegar. Part I. Spirit, Artificial, Malt, and Distilled Malt Vinegars and their Differentiation." By F. W. Edwards, F.I.C., and H. R. Nanji, B.Sc., Ph.D., D.I.C., F.I.C.

"The Detection and Determination of Ouabain and Strophanthin." By W. D. Raymond, B.Sc., A.I.C.

"A New Colour Reagent for Lead and its Uses as an Indicator in the Titration of Various Cations and Anions." By B. S. Evans, M.C., D.Sc., F.I.C.

"A New Iodine Method for the Determination of Starch. Part V." By J. J. Chinoy, M.Sc., Ph.D., F.I.C.

"The Determination of Cobalt in Animal Tissues." By K. J. NcNaught.

"The Determination of Nitrogen in Mixed Fertilisers containing Nitrates and Chlorides." By Bernard Dyer, D.Sc., F.I.C., and J. Hubert Hamence, Ph.D., M.Sc., F.I.C.

"The Determination of Acid in Wool." By J. Barritt, B.Sc., A.I.C., H. H. Bowen, F. L. Goodall and A. Whitehead.

"The Vitamin-A and -D Contents of Butter. II. Seasonal Variation." By H. Wilkinson, B.Sc., Ph.D.

"Cacao Shell in Cocoa and Cacao Products." By H. C. Lockwood, B.Sc., F.I.C.

"The Selective Oxidation of Animal and Vegetable Fats: A new Constant." By W. A. Alexander, B.Sc., A.I.C.

"The Estimation of the Essential Oils of White and Brown Mustards." By R. C. Terry, M.Sc., A.I.C., and J. W. Corran, Ph.D., F.I.C.

"The Electrolytic Determination of Bismuth." By F. G. Kny-Jones, M.Sc.

The February meeting was a joint meeting with the Food Group of the Society of Chemical Industry, at which the following contributions were given on the subject of The Analysis and Differentiation of the Composition of Iron, Phosphorus and Calcium Compounds in respect of Nutritional Requirements.

General Introduction by Professor J. C. Drummond, M.C., D.Sc., F.I.C.
Iron Compounds by R. A. McCance, M.A., Ph.D., M.D., M.R.C.P., M.R.C.S.
Phosphorus Compounds by Professor H. D. Kay, O.B.E., D.Sc.
Calcium Compounds by Professor E. C. Dodds, M.V.O., D.Sc., M.D., F.R.C.P., and J. D. Robertson, M.D., Ch.B., D.P.H.

THE ANALYST.—During the year THE ANALYST continued its forward progress; it contained 919 pages as compared with 914 in 1937. Forty-six papers were published, and these can be classified into 14 on food and drugs, 11 relating to organic chemistry, 15 on inorganic and metallurgical subjects, 2 on water analysis, and 5 on subjects relating to toxicology, including the masterly survey of certain narcotic drugs given by the outgoing President (Dr. Roche Lynch) in his Address. These figures show that the journal is being increasingly used as the scientific medium for papers on inorganic analysis. An outstanding instance was the publication, for the Department of Scientific and Industrial Research, of the paper by Sir Gilbert Morgan and Dr. G. R. Davies on the gravimetric determination of germanium.

Twenty-five notes on analytical and kindred subjects were published, and here again the range was wide, for the notes can be classified into 9 on food and drugs, 8 organic, 6 inorganic, and 2 on physical subjects.

As in former years, the Dominion Analysts have sent their reports and useful material has been abstracted from these. Reports have also been received from State Departments and Experimental Stations in the United States, and the Editor has received letters from the chemists of these Departments thanking the Society for the notice given to them.

HON. TREASURER'S REPORT.—The Hon. Treasurer reports that the financial position of the Society continues to be satisfactory, income more than balancing expenditure.

VISIT TO SOUTH EASTERN AGRICULTURAL COLLEGE, WYE, KENT.—On Friday, June 10th, members of the Society visited the South Eastern Agricultural College, by kind invitation of the Principal. A tour of the College premises and grounds was made, the objects of interest including the Dairy Herd, the Veterinary Research Laboratory, Commercial Poultry Plant, Pig Husbandry Research Station, Commercial Horticultural Section and the College buildings.

FOOD AND DRUGS BILL (now the Food and Drugs Act, 1938).—The President, Mr. F. W. F. Arnaud and Dr. H. E. Cox represented the Society at the meetings of the Joint Select Committee of the Houses of Parliament. Some important alterations were made in the Bill at the request of the representatives of the Society and are now embodied in the new Act.

AIR RAID PRECAUTIONS.—At the request of the Air Raid Precautions Department of the Home Office, a provisional Memorandum on Gas Detection and Identification Service was submitted to careful consideration by the Council, and a Report on the utilisation of the services of chemists in this connection was sent to the Home Office.

CONGRATULATIONS.—The Council has congratulated Dr. C. A. Seyler on the conferment of the D.Sc. degree (*honoris causa*) by the University of Wales.

ANALYTICAL METHODS COMMITTEE.—Although no reports have been published by the Committee during the year, substantial progress has been made in the work of some of its Sub-Committees, enabling reports to be drafted, the early publication of which may be expected.

A new Sub-Committee has been appointed, under the chairmanship of Professor T. P. Hilditch, to consider the standardisation of a Method for the Determination of Unpolymerisable Matter in Oils with especial reference to Tung Oil.

The Committee has to deplore the loss by death of Mr. G. Nevill Huntly. As his successor on the Committee, the Council has appointed Dr. A. D. Mitchell.

ANALYTICAL INVESTIGATION SCHEME.—One paper, "The Analysis of Vinegar, Part I," by F. W. Edwards and H. R. Nanji, has been published in THE ANALYST, 1938, **63**, 410, and there are three subjects now under investigation.

NORTH OF ENGLAND SECTION.—Five meetings have been held during the year. Eight papers have been read and one discussion held.

"The Chemical Analysis and Physical Testing of Refractories." By W. J. Rees, M.Sc., F.I.C.

"A Note on Nigerian Ginger." By P. H. Jones, F.I.C.

"The Determination of Mercury with Special Reference to some Pharmaceutical Preparations." By H. Brindle, B.Sc., F.I.C., and C. E. Waterhouse, A.I.C.

"The Estimation of Vitamins and Hormones." By R. A. Morton, Ph.D., D.Sc., F.I.C.

"A Note on the Behaviour of Rice Bran." By C. Loudon, B.Sc., F.I.C., and F. L. Kinsella.

"A Convenient Method of Estimating the Hydrocyanic Acid Generated by Linseed Cake." By C. Loudon, B.Sc., F.I.C., and H. Antrobus.

"On the Composition and Analysis of Hair Dyes." By H. E. Cox, D.Sc., Ph.D., F.I.C.

Discussion introduced by the President (Prof. W. H. Roberts, M.Sc., F.I.C.) on "The Food and Drugs Act, 1938."

The Annual Address by the Chairman (Professor T. P. Hilditch, D.Sc., F.I.C.) on "Speed Limits in Analytical Matters."

Attendances at meetings have been maintained up to the standard of previous years. The President has attended several meetings.

The ninth Summer Meeting, held at Scarborough in June, was very successful. Dr. G. Roche Lynch gave the paper. There was a very good attendance and the meeting afforded many opportunities for members to fraternise.

Nine candidates have applied for membership of the Parent Society through the Section.

One hundred and five subscriptions have been paid for the year, an increase of seven on the highest previous year.

The Honorary Secretary acknowledges with thanks the support of the Chairman, Officers and Members of the Committee in the working of the Section throughout another year.

SCOTTISH SECTION.—Three meetings were held in the year, at which the following papers by members of the Section were read and discussed:

"The Bakery Chemist's Point of View." By H. C. Moir, B.Sc., A.I.C.

"The Manufacture of Condensed Milk." By G. R. Howat, B.Sc., Ph.D.

"The Proportion of Copper present in Tomato Purée." By T. Cockburn, F.I.C., and M. Herd, B.Sc., F.I.C.

"The Estimation of the Organic Acids and Protein Decomposition Products in Silage." By A. M. Smith, Ph.D., D.Sc.

"The Estimation of Small Quantities of Gold in Urine." By A. R. Jamieson, B.Sc., F.I.C., and R. S. Watson, A.I.C.

"The Determination of Alumina in Water." By R. T. Thomson, F.I.C.

Thirty-nine subscriptions were received, an increase of five over the previous year. Eight new members joined the Parent Society through the Section and two members resigned on taking up residence outside the Scottish area.

With the passing of the Food and Drugs Act, 1938, which applies mainly to England, the Chairman and Hon. Secretary, on behalf of the Section, and with the consent of the Council of the Parent Society, addressed a letter to the Department of Health for Scotland, requesting that a similar Food and Drugs Bill be drafted for Scotland.

CONGRESSES, ETC.

Tenth International Congress of Chemistry, Rome, 1938.—The Society was represented by the President with Mr. A. H. Bennett, Dr. J. J. Fox, Dr. L. H. Lampitt, and Sir R. Robertson.

Royal Sanitary Institute Congress, Portsmouth, 1938.—The Society was represented by Mr. F. W. F. Arnaud and Mr. R. P. Page.

Rubber Technology Conference, London, 1938.—The Society was represented by Dr. P. Schidrowitz.

The Council desires to record its thanks to the members of the Society who have served on the Committees and Sub-Committees and to those who have represented the Society on other bodies.

W. H. ROBERTS, *President*
LEWIS EYNON, *Hon. Secretary*

The Practical Treatment of Dairy Effluents

BY C. A. SCARLETT, B.Sc., A.K.C., F.I.C.

(*Read at the Meeting of the North of England Section, December* 11, 1937)

THE question of the treatment of dairy effluents is one that has come very much to the fore in recent years, and a survey of the literature on the subject indicates that many attempts have been made to find a solution to this problem. Barritt[1] refers to an excellent summary of these methods by McDowall. They include among others:—(1) Land seepage. (2) Sedimentation. (3) Chemical precipitation. (4) Filtration through sand. (5) Biological treatment in septic tanks. (6) Biological treatment in contact beds. (7) Biological treatment on percolating filters. (8) Biological oxidation by the activated sludge process. (9) Various combinations of these processes.

The most common methods employed at milk factories in this country appear to involve preliminary treatment in tanks under aerobic or anaerobic conditions, followed by some kind of filtration through sand or coke or over biological filters.

Methods involving anaerobic conditions usually result in complaints due to the highly objectionable odours arising from the scum of decomposing fat and protein matter that forms on the surface of the holding tanks and filters. To overcome this trouble chlorine is sometimes added, but this usually results in the plant becoming practically sterile and useless as a purifying agent, the waste liquor passing through it with very little change except for mere mechanical filtration and subsequently creating a nuisance by polluting the brook or stream into which it flows.

In an attempt to remedy this difficulty of the formation of a scum on tanks and filters, the holding period is sometimes reduced to a minimum, the tank merely acting as a balancing tank to give a constant supply of liquid to the filters. Two filters are then used in series and connected so that either can be a primary or secondary. When clogging and ponding occur on the primary filter, owing to deposition of protein and fat, the order of filtration is reversed, the primary filter becoming the secondary and receiving partially purified liquor which oxidises the scum on its surface. This method depends for its success on the provision of a plant of adequate capacity to deal with the volume of waste produced, so that the oxidation of the scum can be completed before fresh deposits are built up on the primary bed. A further objection to this method of alternating filtration may be that a primary bed which has developed its own organisms to deal with a liquid of a certain strength is suddenly called upon to purify a much weaker or stronger liquid, as the case may be, a procedure which might disturb the bacterial and other life in the bed and so upset its purifying capacity until the organisms have adapted themselves to the new conditions.

When sand filtration or land seepage is employed, clogging eventually occurs, owing to deposition of protein and fat, and fresh areas have to be provided until the original areas recover. In those plants working under aerobic conditions, it is essential that the sludge be removed daily in order to prevent its anaerobic decomposition during periods of settling, otherwise the odour may become a nuisance.

When the waste liquors are treated by the activated sludge process there are at least two methods of achieving aeration. In the Kessener method described by Rudolf,[2] lime is added to neutralise any acidity present and aeration is obtained by means of revolving brushes. Effluents of good quality are reported to have been produced by this process.

In the activated sludge plant at Ellesmere[3] aeration is obtained by blowing air through porous plates and the crude liquors are diluted with purified effluent before treatment. Strict control of working conditions is essential if satisfactory results are to be obtained by this method.

In this paper a method of treatment is described, based on storage of the waste liquors under controlled conditions during which fermentation occurs, with separation of fat and casein, sedimentation of the separated material and biochemical treatment of the clear supernatant liquor on percolating filters.

The waste liquors from a milk depot engaged in brine cooling, pasteurising and sterilising milk, butter-making, cream-bottling and condensing, will consist of a dilute solution of milk slightly alkaline in character by reason of the detergents used in washing down and cleaning of the plant, and containing more or less sucrose according to the amount of sweetened milk produced. The amount of milk in these wastes varies, but it usually lies between 0·5 and 2 per cent., being on the average under 1 per cent. If such a liquid is stored its *p*H will change, owing to fermentation of the lactose, the rate of change depending on the temperature of the liquid, and the amount of change on the quantity of alkali present.

Our own experiments on the fermentation of 1 per cent. milk solutions of varying *p*H under different conditions of temperature and aeration, together with the published results of other workers making similar experiments, lead to the following conclusions:

At about 4° C. the liquid is quite stable and no fermentation occurs for days.[4] At about 10° C. fermentation soon sets in and reaches a maximum between 25° and 35° C., ceasing again between 45° and 50° C.

The lactic acid bacilli chiefly responsible for this fermentation are facultative, *i.e.* they will grow under either aerobic or anaerobic conditions. Under anaerobic conditions other changes occur including proteolysis, and the decomposition products include substances of highly disagreeable odour, such as nitrogen bases of the indole or skatole types, which are objectionable in the vicinity of a dairy.

If the *p*H falls to 4·5 practically all the casein separates out, taking the fat with it,[5] and the fermented liquor can be kept for a further period under anaerobic conditions without appreciable change. If the *p*H is about 5·5 most of the fat but less protein separates, and if the liquid is stored for a further period the *p*H may increase and some of the precipitated protein may redissolve.

The Biological Oxygen Demand (B.O.D.), or dissolved oxygen absorbed in 5 days at 65° F., of the clear fermented liquor is lower than that of the original liquid, but if the *p*H increases and protein redissolves the B.O.D. will increase. There is thus no advantage in holding the liquid for too long a period if it is to undergo biological treatment later. Also, from the practical point of view, the shorter the period during which the liquid is held, the less chance there will be of protein decomposition, with the formation of nauseating odours. Continuous aeration of the liquid will prevent this protein decomposition to a certain extent, as it is essentially an anaerobic process. Intermittent aeration, however, will permit the formation of protein decomposition products when the aeration is stopped, and, on re-starting, the objectionable gases produced will be discharged.

Under proper conditions of aeration and temperature control, it was found that fermentation of a 1 per cent. milk solution was complete in less than 24 hours, and the separated solids showed no tendency to form a scum but rapidly fell to the bottom of the tank when aeration was stopped, the supernatant liquid being practically clear and containing only traces of suspended matter. This clear supernatant liquor can be run over percolating filters at a rate not exceeding 100 gallons per cubic yard per day,[5] with the production of an effluent that will have a B.O.D. less than 2. The filter is not likely to become clogged as there is nothing in the liquor to separate, the casein having already been removed.

The temperature at which the required changes were brought about in the shortest time was found to be about 30° C. and the best condition was that of continuous aeration or agitation to prevent the formation of a surface scum.

The plant required to treat a dairy waste on these lines consists essentially of a tank large enough to hold a day's output of effluent and supplied with the necessary equipment to hold the contents at the required temperature and to keep them in a state of constant agitation, together with percolating filter beds of sufficient capacity to deal with the volume of effluent produced.

Fig. 1 represents a diagrammatic flow sheet of the plant of which the following is a description:—A is a common collecting tank to which all drains are led. It is well sloped at the bottom, being 12 ft. deep at the centre and 10 ft. at the sides. It can hold about 2000 galls. and is provided with two automatic non-clog type pumps which pump the effluent into the holding or balance tank.

The effluent before entering this collecting tank passes through a strainer, B, of the basket type, which removes paper, matches and other larger sized material of similar nature. This strainer can be hauled up by means of lifting tackle for cleaning purposes.

The holding or fermentation tanks, C, are funnel-shaped and two in number. Each holds over 30,000 galls. or one day's supply of effluent. The top portion is approximately 20 ft. square and 10 ft. deep, and the funnel portion 10 ft. deep at the centre. These tanks are fitted with pipes, H, for blowing in air, and a steam-coil, J, about half-way down the funnel. There is an outlet, K, at the bottom of each tank for running off the sludge and a pipe through which any remaining liquor is returned to the collecting tank, A. Three outlets are provided for tapping off the liquid, one 7 ft. from the bottom of the funnel, another 5 ft. above this, and the third 5 ft. above the second. These allow the liquid to be run off as soon as possible, so that there is no necessity to wait until the suspended matter has settled to the bottom of the tank.

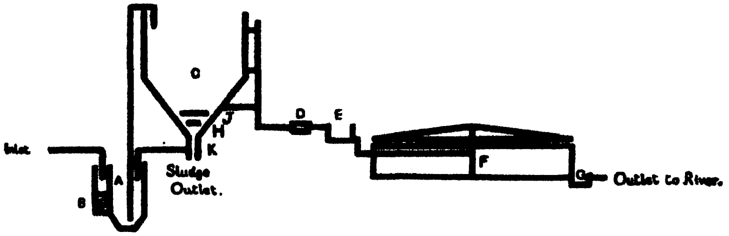

Fig. 1

From the fermentation tank the effluent passes through one of a pair of strainers, D. These consist of perforated cylinders of metal enclosed in cylindrical mats of coconut fibre, like large extraction thimbles. Any light suspended matter remaining in the liquid is removed during passage through these strainers.

From the strainer the liquid enters the syphon, which provides an intermittent flow over the beds, and consists of a small iron tank which has a capacity of about 225 galls., the inlet pipe being fitted with a valve controlled by a ball-cock.

The two filter beds, F, are 36 ft. in diameter and 6 ft. deep, and they work in parallel. The total volume of filtering medium is 452 cubic yards, which at a rate of 4 galls. per cubic yard per hour gives a filtering time of 16 hours for 30,000 galls. In actual practice the rate has always been higher than this, the day's supply of effluent usually being filtered in about 11 hours. The final effluent from the filters passes into a small sump, G, used as a sampling chamber and then through a 9-inch pipe to the stream, which it enters at the overflow of a dam about 100 yards lower down, so that excellent mixing with the river water is obtained. Room has been left for the installation of grit and detritus tanks if they are required.

The working of the plant is as follows:—The mixed effluent, after rough screening by passing through the basket filter, enters the collecting tank and is pumped into one of the fermentation tanks. Each of these holds a day's supply of effluent, so that, under working conditions, one tank is being filled while the other is emptying. The pumps are automatic and the timing is so arranged that the collecting tank is kept as empty as possible to prevent the occurrence of decomposition and fermentation in it. In the fermentation tank aeration is continuous by means of a compressor blowing air through the perforated pipes and the steam-coil is automatically controlled to maintain the temperature at 30° C. On the following morning the steam and air are cut off, and the separated material quickly settles to the bottom of the tank. The practically clear supernatant liquor is then allowed to flow to the syphon, which has a working cycle of 10 minutes, being filled in four minutes and emptied in six. In this time approximately 400 galls. of effluent are passed over the beds, although the capacity of the syphon is only 225 galls. This is due to the fact that as the level of the liquid drops, the ball-cock falls and opens the valve on the inlet pipe, thus allowing more effluent to enter. As the outlet from the syphon is, however, larger than the inlet, the level of the liquid continues to fall until a certain point is reached when the outlet automatically closes and the syphon refills.

When the level of the liquid in the fermentation tank has dropped to that of the bottom tapping, about 3000 galls. are left. This contains the sludge which at the present time is run off into churns and spread on the land. Owing to the settling that has occurred, the whole of the sludge is removed in 3 to 4 churns, each of 17 galls. capacity. The remaining liquid is run off into the collecting tank and pumped up into the other fermentation tank, thereby "seeding" it to a certain extent.

The empty fermentation tank, the collecting tank and all pipe lines are washed down daily, and the whole plant is kept in as clean a state as possible. As a result of this there has been no nuisance from the odour of decomposing protein. The volume of effluent passing over the filters is about 30,000 galls. per day. At this rate a liquid with an average B.O.D. of 40 gives an effluent with a B.O.D. less than 1.

In the experiments carried out at Ellesmere by the Water Pollution Research Board during the period of August, 1935, to March, 1936,[3] the milk wastes leaving the primary sedimentation tank had an average B.O.D. of 70, and were diluted with about 4 times their volume of purified effluent to reduce the B.O.D. to about 20 before filtering at a rate of 80 galls. per cubic yard per day. The average B.O.D. of the final effluent was 0·7. This method of diluting the tank liquor to reduce its B.O.D. would be extremely uneconomical in practice, as it involves filtering 5 times as much liquid as the dairy produces daily in effluent. In later experiments the rate of flow was increased to 120 galls. per cubic yard of filtering medium per day without any deterioration in the quality of the effluent being observed.[3] Even when the rate was increased to 160 galls. per cubic yard per day there appeared to be little change in the quality of the final effluent.

However, even this high rate of flow only represents the equivalent of 32 galls. per cubic yard per day, based on the original effluent, owing to the dilution that has taken place, compared with the 130 galls. per cubic yard per day used in the plant here described.

Typical results obtained on our tank liquors, before and after aeration, and on the final effluent are shown in Table I. (The methods of analysis used are those recommended by the Ministry of Health in their 1929 issue of *Methods of Chemical*

Analysis as Applied to Sewage and Sewage Effluents, except for nitrates, for which the method employed was a modification of that suggested by Vey,[6] depending on the formation of 5-nitro-2.4-xylen-1-ol, which is volatile in steam and gives a highly coloured solution in dilute sodium hydroxide). The degree of purification obtained is shown as a percentage based on the B.O.D. The figures in brackets are calculated on the original crude liquor and indicate a purification of at least 99 per cent. The figures given for the "strength" of the various liquors are calculated from McGowan's formula : (Ammon. + organic N) × 4·5 + (Oxygen absorbed in 4 hours × 10·4). They are, of course, only approximate, but are introduced to illustrate how purification proceeds.

TABLE I

TYPICAL ANALYSES OF TANK LIQUORS AND EFFLUENT

No.:	Crude tank liquor M5012	Aerated tank liquor M5013	Final efflu-ent M5014	Crude tank liquor M4350	Aerated tank liquor M4351	Final efflu-ent M4352	Crude tank liquor M5714	Aerated tank liquor M5766	Final efflu-ent M5767
Suspended solids ..	39	7·5	2·5	46	4	3	23	4	2·5
Organic suspended solids	33	6·5	1·5	43	3·5	3	19·5	3·5	2·5
Total solids	148	92	64	158	92	64	104	64	52
Loss on ignition of total solids	90	40	10	100	40	10	60	20	8
Mineral ash	58	52	54	58	52	54	44	44	44
Dissolved solids ..	109	84·5	61·5	112	88	61	81	60	49·5
B.O.D. dissolved oxygen absorbed in 5 days ..	77	41	0·92	80	37	0·68	41	13	0·24
Saline ammonia ..	0·03	1·08	0·002	0·06	0·43	0·003	0·028	0·42	0·006
Albuminoid ammonia	1·8	0·72	0·11	1·9	0·8	0·16	1·04	0·42	0·12
Nitrous nitrogen ..	nil	nil	nil	nil	nil	nil	nil	nil	nil
Nitric nitrogen ..	nil	nil	0·44	nil	nil	0·38	nil	nil	0·63
Combined chlorine ..	3·7	3·7	4·6	7·0	7·0	6·1	3·3	3·3	3·0
Oxygen absorbed from $N/80$ $KMnO_4$,									
in 3 minutes ..	1·8	1·18	0·12	—	—	—	1·22	0·64	0·10
in 4 hours ..	6·9	2·65	0·34	6·4	2·25	0·41	4·25	1·55	0·31
*p*H	6·4	6·6	8·3	6·0	6·6	8·3	6·3	6·8	8·1
Total nitrogen ..	4·37	2·6	0·59	3·89	1·75	0·63	—	—	—
Organic nitrogen ..	4·35	1·71	0·15	3·84	1·4	0·25	—	—	—
Strength	91	39	4	84	31	5	—	—	—
Percentage purification based on B.O.D. of:									
(1) Aerated tank liquor	—	—	98	—	—	98	—	—	98
(2) Crude tank liquor	—	(46)	(99)	—	(53)	(99)	—	(68)	(99)

Results expressed in parts per 100,000 except where otherwise stated.

As the tank liquor after aeration has had most of its suspended solids removed by sedimentation in the fermentation tank, it was thought that it might be interesting to observe the effect produced by filtering the crude tank liquor through paper and comparing the analysis of the filtrate with that of the aerated liquor.

Table II shows some of the results obtained. From these it would appear that in this particular instance, simple removal of the suspended solids of the crude tank liquor produced 30 per cent. purification based on the B.O.D., whereas aeration and sedimentation produced 37 per cent. purification on the same basis. The removal of the 3 parts of suspended solids remaining in the aerated liquor by filtration through paper resulted in a liquid showing 53 per cent. purification based on the B.O.D. of the original crude tank liquor.

TABLE II

TABLE SHOWING THE PURIFICATION EFFECTED BY FILTERING THE TANK LIQUORS

No.:	Tank liquor M5504	Tank liquor after filtering in Lab. M5504	Tank liquor after aeration M5518	Aerated tank liquor after filtering in Lab. M5518	Final effluent M5519
Suspended solids	17	nil	3	nil	2
Organic suspended solids	14·5	—	2·5	—	—
Total solids	128	—	82	—	54
Loss on ignition of total solids ..	82	—	38	—	10
Mineral ash	46	—	44	—	44
Dissolved solids..	111	—	79	—	42
Dissolved oxygen absorbed in 5 days, B.O.D.	56	39	35	26	0·78
Saline ammonia	0·050	0·046	0·45	0·42	0·002
Albuminoid ammonia	1·44	0·88	0·64	0·48	0·13
Nitrous nitrogen	present	present	absent	absent	absent
Nitric nitrogen	absent	absent	absent	absent	0·6
Combined chlorine	4·2	4·2	4·1	4·1	3·8
Oxygen taken up from $N/80$ $KMnO_4$ in:					
(1) 3 minutes	1·32	0·98	0·96	0·74	0·12
(2) 4 hours..	3·9	2·9	3·75	2·93	0·35
Total nitrogen	3·35	2·56	1·85	1·32	0·76
Organic nitrogen	3·31	2·48	1·48	0·97	0·16
Strength	56	42	47	36	4
*p*H	6·9	—	6·3	—	—
Percentage purification based on B.O.D. of:					
(1) Aerated tank liquor	—	—	—	25	98
(2) Crude tank liquor	—	(30)	(37)	(53)	(99)

Results expressed in parts per 100,000 except where otherwise stated.

Aeration and effective removal of suspended solids appear to account for half the purification effected on the basis of the B.O.D., but only about 25 per cent. on the permanganate figures.

The effect of the aeration is shown more clearly by comparing the two paper-filtered samples. There is a drop in the total nitrogen, albuminoid ammonia and B.O.D. figures and an increase in the saline ammonia, indicating that the process does bring about some improvement in the quality of the liquid.

TABLE III

FINAL EFFLUENT BEFORE AND AFTER FILTERING IN LABORATORY

No.:	Before M3449	After M3449	Before M3765	After M3765
Suspended solids	5	nil	3	nil
Total solids	74	68	70	66
Loss on ignition of total solids	14	8	12	10
Dissolved oxygen absorbed in 5 days, B.O.D. ..	0·51	0·22	0·90	0·63
Saline ammonia	0·010	0·011	0·013	0·013
Albuminoid ammonia	0·21	0·056	0·16	0·068
Oxygen taken up from $N/80$ $KMnO_4$ in 4 hours ..	0·45	0·24	0·36	0·23
Percentage purification based on B.O.D. of crude tank liquor	98	99·2	96	97·5

Results expressed in parts per 100,000 except where otherwise stated.

On several occasions the final effluent was found to contain more than 3 parts of suspended solids per 100,000. This was obviously due to the absence of a humus tank large enough to give efficient settling.

Table III shows the effect of removing these suspended solids in the final effluent by filtration through paper. The albuminoid ammonia is reduced by about 60 per cent. and the B.O.D. and oxygen absorbed from permanganate by about 30 per cent. The provision of a humus tank of at least 4 hours' holding capacity would, therefore, bring about considerable further improvement in the quality of the effluent.

After the plant had been working for about eight months the rate of flow was increased and Table IV shows the effect of this on the beds and on the quality of the final effluent.

TABLE IV

VARIATIONS IN FINAL EFFLUENT DUE TO INCREASING THE RATE OF FLOW OVER THE FILTER BEDS

No.:	M7317	M8478	M8523	M8828	M9147	M9497	M9498	N211 (80)	N308 (128)	N664 (24)	N1917 (36)
Suspended solids ..	3·6	3	2·5	2·5	3·5	11	7	10·5	14·5	5	2·5
Dissolved oxygen absorbed in 5 days, B.O.D.	0·5	0·5	0·35	1·3	1·4	4·3	2·2	(165) 5·3	(170) 3·1	(105) 1·5	(90) 0·52
Saline ammonia ..	0·001	0·013	0·018	0·32	0·035	0·2	0·011	0·11	0·066	0·048	0·016
Albuminoid ammonia	0·112	0·088	0·096	0·18	0·19	0·45	0·35	0·50	0·52	0·19	0·096
Nitrous nitrogen ..	abs.	abs.	abs.	pres.	pres.	abs.	abs.	abs.	pres.	pres.	pres.
Nitric nitrogen ..	0·65	0·27	0·18	0·57	0·25	abs.	abs.	abs.	0·63	1·7	1·4
Oxygen taken up from $N/80$ $KMnO_4$ in: (1) 3 mins. ..	0·11	0·088	—	—	—	—	—	—	—	—	—
(2) 4 hrs. ..	0·13	0·26	—	—	—	—	—	—	—	—	—
Percentage purification based on B.O.D. of crude tank liquor	99	—	—	—	—	—	—	96	98	98·7	99
*p*H	8·0	8·1	8·0	7·4	7·6	7·6	7·6	7·7	7·9	7·8	8·0

Figures in brackets refer to corresponding crude tank liquor.
Results expressed in parts per 100,000 except where otherwise stated.

The main points noticeable are:

(1) A considerable increase in the amount of suspended solids. (When the rate was about double that normally used, much of this appeared to be inorganic, indicating the possibility of erosion of the filtering medium.) (2) An increase in the albuminoid ammonia and B.O.D. (3) A decrease in the amount of nitrates produced. These eventually disappeared when the rate was double that normally used. (4) A drop in the *p*H.

All these results indicate a considerable falling off in the ability of the beds to purify the volume of effluent passing through them. The maximum rate reached was about 250 galls. per cubic yard per day, compared with a normal rate of 130 galls. per cubic yard per day. On reducing the rate to its normal figure the beds rapidly recovered, and the analysis of the final effluent went back to normal.

Table V shows some analyses of the river water before and after the erection of the effluent plant. The first two columns show the condition of the river before and after receiving the crude waste without treatment. Note the increased values for B.O.D., albuminoid ammonia and oxygen absorbed from $N/80$ $KMnO_4$, all of which indicate the adverse effect produced on the stream.

TABLE V

No.:	River water above dairy J3479	River water below dairy J3480	River water above dairy M462	River water below dairy M4103	River water below dairy M4644	River water below dairy N5456
Suspended solids	0·4	2·0	1·0	1·0	0·5	0·5
Total solids	41	44	34	33	—	—
Dissolved oxygen absorbed in 5 days, B.O.D.	0·17	0·51	0·24	0·32	0·16	0·2
Saline ammonia	0·046	0·022	0·068	0·066	0·014	0·015
Albuminoid ammonia	0·02	0·036	0·029	0·026	0·021	0·019
Nitrous nitrogen	trace	trace	absent	absent	present	absent
Nitric nitrogen	0·3	0·3	0·28	0·28	0·35	0·38
Oxygen taken up from $N/80$ $KMnO_4$ in 4 hours	0·086	0·12	0·20	0·21	0·16	0·11
*p*H	7·3	7·4	7·3	7·2	7·8	7·8

Results expressed in parts per 100,000 except where otherwise stated.
First two samples taken before installation of effluent plant.
Last four samples taken after installation of effluent plant.

The last four columns show the condition of the river before and after receiving the effluent from the plant. There is little significant difference between them.

SUMMARY.—A method of treating milk wastes has been described in which the crude liquors are held under prescribed conditions of temperature and aeration, allowed to settle, and then run over biological filters at a rate of 130 galls. per cb. yard per day.

Only primary filtration is used and over a period of 14 months the beds have remained perfectly clean, no clogging or ponding having occurred.

The final effluent produced is clear and bright, free from odour and stable on incubation.

It has an average B.O.D. of about 1, and the purification effected, based on the B.O.D. of the original crude waste, is 99 per cent.

I am indebted to my colleagues, Messrs. H. G. Coles and N. Hurt, for carrying out most of the analytical work involved, and to Mr. A. Glover and the Directors of the C.W.S. for permission to publish these results.

ADDENDUM.—Further experience obtained since this paper was read has been so satisfactory that a plant to deal with over 250,000 gallons a day has been erected and is giving excellent results.

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RESEARCH DEPARTMENT
CO-OPERATIVE WHOLESALE SOCIETY, LTD.
MANCHESTER

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A Rapid Method for the Determination of Parachlorometaxylenol

By D. McNICOLL, M.A., B.Sc., Ph.D., R. P. MERRITT, Ph.C., and
T. F. WEST, M.Sc., F.I.C.

The method proposed by Merritt and West[1] for determining parachlorometaxylenol is satisfactory as regards accuracy but involves a good deal of manipulation. The more rapid methods which we have now developed depend on the fact that, whilst most phenols (especially those of a feebly acidic nature) do not esterify readily, fatty acids readily form methyl esters when naphthalene-β-sulphonic acid is used as catalyst.[2]

After it had been established that this applied to *p*-chloro-*m*-xylenol a number of experiments with the pure phenol were based on this fact, and finally the alternative Methods I and II were adopted. The second method has been shown to yield satisfactory results for each of the solutions previously examined by Merritt and West (*loc. cit.*) which contained a variety of soaps and essential oils. As in the method of these authors, the present processes would not be successful if essential oils containing phenols were included in antiseptic solutions, although this appears unlikely in view of the oils available.

However, by the methods described below the feebly acidic constituents of such solutions are obtained in a practically pure state and the m.p. of the *p*-chloro-*m*-xylenol at this stage was in some instances 112–113° C.

The identity of the phenol in question may be confirmed by recrystallisation from benzene to m.p. 115° C. and by determining the mixed melting-point.

Method I.—Twenty ml. of the antiseptic solution were pipetted into a separator and acidified with 6*N* sulphuric acid. The oily layer was extracted three times with ether (25 ml.), the combined ethereal extracts were washed three times with 10 ml. of water, and the water was washed with ether (15 ml.). The ethereal solutions were united and dried over sodium sulphate and, after removal of the solvent, the residue was boiled for 45 minutes on a hot plate under reflux with 20 ml. of a 4 per cent. solution of naphthalene-β-sulphonic acid in methyl alcohol. The solution was then transferred to a separator with water (2 volumes) and extracted three times with 25 ml. of ether. The ethereal solution was extracted eight times with 25 ml. of *N* sodium hydroxide solution, the alkaline solution was washed with 20 ml. of petroleum spirit, and the petroleum spirit with 10 ml. of *N* sodium hydroxide solution. The combined alkaline extracts were acidified with 6 *N* sulphuric acid, and the liberated phenol was extracted three times with 25 ml. of ether. The ethereal extract was washed with water in the usual way, the solution was dried over sodium sulphate, and, after removal of the solvent, the residue was dried in a vacuum desiccator. The results obtained for solutions I to VI (see Merritt and West, *loc. cit.*) are shown in Table I.

Method II.—After extraction of the fatty acids, phenol and essential oils and esterification as in Method I, the methyl alcohol solution was transferred to a separator with twice its volume of *N* sodium hydroxide solution and 20 ml. of petroleum spirit, and the mixture was vigorously shaken. The petroleum spirit was extracted three times with 10 ml. of *N* sodium hydroxide solution, a little alcohol being used if necessary to break the emulsions formed. The combined alkaline extracts were acidified with 6 *N* sulphuric acid and extracted three times with 25 ml. of ether, the ethereal extract was washed with water in the usual way and dried over sodium sulphate, the solvent was removed, and the residue was dried in a vacuum desiccator and weighed. In some instances the result at this stage was high and accordingly, as a general method, it is preferable to purify the crude phenol by dissolving in the smallest quantity of sodium hydroxide solution, diluting with water to 60 ml., and precipitating with carbon dioxide. The suspended phenol is then extracted with ether, separated, dried in the usual manner and weighed. The results shown in Table II for Solutions I to VI were obtained by including the purification with carbon dioxide in the method.

TABLE I

ANALYSIS OF SOLUTIONS BY METHOD I

	p-Chloro-*m*-xylenol		
Solution No.	Added in 100 ml. g.	Determined in 100 ml. g.	m.p. °C.
I	2·491	2·547	112–113
II	3·500	3·465	108–109
III	3·318	3·290	112–113
*IV	3·078	3·290	108–111
V	3·507	3·543	109–111
*VI	3·339	3·509	106–109

* With solutions IV and VI it was necessary to purify the crude phenol by washing with petroleum spirit. For this reason Method II was developed and found generally applicable.

TABLE II

ANALYSIS OF SOLUTIONS BY METHOD II

	p-Chloro-*m*-xylenol		
Solution No.	Added in 100 ml. g.	Determined in 100 ml. g.	m.p. °C.
I	2·491	2·484	110–111
II	3·500	3·497	112–114
III	3·318	3·307	110–111
IV	3·078	3·098	109–110
V	3·507	3·522	113–114
VI	3·339	3·392	107–109

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THE BRITISH OIL AND CAKE MILLS, LTD.
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LONDON, N.1

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The Micro-Electrolytic Deposition and Determination of Arsenic

By SYDNEY TORRANCE, A.R.C.S., B.Sc., D.I.C.

No gravimetric electrolytic method for the determination of arsenic on a micro-chemical scale has yet been published. The following is an adaptation of the author's method previously described[1] for ordinary scale electrolytic determinations of arsenic; it is based on the Reinsch test and consists in depositing arsenic as an alloy with copper from a solution containing about 15 per cent. of conc. hydrochloric acid, the cathode potential being controlled by means of a saturated-calomel auxiliary electrode. Further work has shown that the method is readily adaptable to micro-quantities of arsenic, the Lindsey–Sand micro-electrolytic apparatus and technique[2] being employed. Lindsey[3] has found that copper may be completely deposited from an acid chloride solution with an anode-to-cathode potential of 0·7 volt, when the electrolysis is carried out at a temperature of 65° to 70° C., hydrazine being present as a depolariser. This was confirmed for solutions of copper alone, even with the high acid-strength utilised, but with the addition of arsenic, it was found necessary to raise the anode-to-cathode potential to 0·9 volt, in order completely to deposit the copper.

Standard solutions of copper and tervalent arsenic were prepared by dissolving AnalaR copper sulphate in water, and pure arsenious oxide in sodium hydroxide solution and acidifying with hydrochloric acid. The standard solutions contained about 1 mg. of copper and 0·1 mg. of arsenic per ml. respectively. The copper solution was standardised by electrolysis, whilst the amount of arsenic in the arsenic solution was calculated from the weight of arsenious oxide taken. Five ml. of each solution were introduced into an electrolysis vessel, and 1·5 ml. of hydrochloric acid (sp.gr. 1·16) and 6 drops of 50 per cent. hydrazine hydrate were added. The mixture was electrolysed at a temperature of 65° to 70° C., with an anode-to-cathode potential of 0·9 volt. The initial current of about 100 milliamps fell to about 10 milliamps within 4 minutes. The electrolysis was continued for a further 5 to 10 minutes, and the copper and arsenic deposit was washed, dried and weighed. It was found that the arsenic was completely deposited with the copper. Results of several similar depositions obtained with a constant ratio of copper to arsenic of 10 : 1 are given in Table I.

TABLE I

Arsenic taken mg.	Copper added mg.	Copper and arsenic deposited mg.	Arsenic found mg.
0·53	4·95	5·49	0·54
0·53	4·95	5·48	0·53
0·53	4·95	5·48	0·53
0·21	1·98	2·20	0·22
0·21	1·98	2·20	0·22
0·11	0·99	1·10	0·11
0·11	0·99	1·10	0·11

Depositions were next made with decreasing ratios of copper to arsenic in order to ascertain the smallest ratio necessary to deposit all the arsenic simultaneously with the copper. From the results given in Table II, it would appear that the minimum ratio is 4 : 1.

TABLE II

Arsenic taken mg.	Copper added mg.	Copper/ arsenic ratio	Copper and arsenic deposited mg.	Arsenic found mg.
1·06	4·95	5	6·02	1·07
0·53	1·98	4	2·51	0·53
0·53	0·99	2	1·46	0·47
1·06	1·98	2	2·89	0·91
1·06	2·97	3	3·93	0·96
1·06	2·97	3	3·92	0·95

A standard solution of quinquevalent arsenic was prepared containing 0·25 mg. of arsenic per ml., by evaporating to fuming a mixture of 0·330 g. of arsenious oxide with 10 ml. of nitric acid (sp.gr. 1·42) and 5 ml. of sulphuric acid (sp.gr. 1·82) in a Kjeldahl flask. When the solution was cool, 0·2 g. of hydrazine sulphate was added, the mixture was evaporated again to fuming, and the solution was diluted to 1 litre. Two ml. of this solution were electrolysed with 5 ml. of the standard copper solution, in the presence of hydrochloric acid and hydrazine, as described above. As had been previously discovered with larger amounts (*loc. cit.*[1]), all the copper, but no arsenic, was deposited. A further portion of the arsenic was reduced in an electrolysis tube by adding to it 1 ml. of a saturated solution of sulphur dioxide. The tube was corked and placed in a boiling water-bath for 5 minutes. The reduced arsenic solution was then electrolysed in the usual manner with copper, hydrochloric acid and hydrazine. All the arsenic was found to have been deposited with the copper. Results of several determinations are given in Table III.

TABLE III

Arsenic taken mg.	Copper added mg.	Copper and arsenic deposited mg.	Arsenic found mg.
0·50	4·95	5·46	0·51
0·50	4·95	5·45	0·50
0·50	4·95	5·45	0·50
1·25	4·95	6·18	1·23
1·25	4·95	6·19	1·24
1·25	4·95	6·19	1·24
0·25	1·98	2·23	0·25
0·25	1·98	2·23	0·25

I wish to thank Dr. Lindsey for his interest in this work, and Imperial Chemical Industries, Ltd., for a grant which has been used to purchase part of the apparatus employed in this investigation.

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The Analysis of Linseed Oils of Various Origins

BY F. NEVILLE WOODWARD, B.Sc.

PRIOR to the introduction by Kaufmann,[1] in 1925, of the thiocyanogen method for the estimation of linolenic, linolic and oleic acids in the presence of each other, only a very few reasonably complete analyses of linseed oil or linseed oil fatty acids had been published.

These published analyses are summarised in Table I.

TABLE I

	Fatty acids, per cent.				Glyceryl radicle Per Cent.	Unsap. matter Per Cent.
	Saturated	Oleic	Linolic	Linolenic		
Hazura and Grüssner[2]	10	5	15	15–α 55–β	—	—
Fahrion[3]	9·3	17·5	30·0	38·0	4·6	0·6
Friend[4]	10·0	5·0	59–48	21–32	4·6	—
Coffey[5]	8·1	5·0	48·5	34·1	4·3	—
Eibner and Schmidinger[6]	8·2	4·5	17·0–α 41·8–β	20·1–α 2·7–β	4·1	1·0

The findings of Hazura and Grüssner are obviously incorrect, as a mixture of the type they suggested would have an iodine value in excess of any found experimentally, whilst Fahrion made the assumption—now known to be untenable—that oleic acid on oxidation could be converted into dihydroxystearic acid in 60 per cent. yield.

Friend's figures represent average values calculated in 1917, and were based on the then existing knowledge of the iodine value and yields of hexabromides obtained on bromination, whilst Coffey estimated the amount of linolenic acid present from the amount of carbon dioxide and volatile acids resulting from the oxidation of linseed oil fatty acids. The investigation of Eibner and Schmidinger gave trustworthy figures for α-linolic and α-linolenic acids, but the values for *iso*linolenic, β-linolic and oleic acids were only approximate, as the only method then available for the determination of these acids in a mixture of all three depended upon the separation of the hexabromostearic acid produced from linolenic acid on bromination of the mixture, and it is now known that this is not a full measure of the linolenic acid originally present.

The most reliable analyses of linseed oil mixed fatty acids published since 1925 are summarised in Table II.

TABLE II

	Fatty acids, per cent.			
	Saturated	Oleic	Linolic	Linolenic
Eibner and Brosel[7] (Calcutta oil)	8·9	18·8	23·2	49·1
Kaufmann and Keller[8] (Plate oil)	9·0	8·0	46·7	36·3
,, ,, (Calcutta oil)	11·3	12·5	54·1	42·1
Gay[9]	10·8	12·4	26·6	50·2
Griffiths and Hilditch[10]	9·7	9·6	42·6	38·1

Eibner and Brosel used Eibner's technique[11] for hexabromostearic acid determination, and checked their results by means of the thiocyanogen method. Kaufmann and Keller's results were calculated on the basis of a thiocyanometric examination, and were later criticised by Gay, who claimed that the thiocyanogen method was unreliable as a means of determining partial unsaturation quantitatively under the conditions stipulated by them; his own recorded values were obtained by the use of a modified technique.

Griffiths and Hilditch analysed linseed oil fatty acids of unspecified origin by three different methods, namely, bromination and separation of hexabromostearic acid, thiocyanogen titration, and the oleic-elaidic transformation method of Hilditch.[10,12] They found that linolenic acid is not completely separable as insoluble hexabromide, but results obtained by the oleic-elaidic transformation (saturated, 9·7; oleic, 9·7; linolic, 42·2; linolenic acid, 38·4 per cent.) fully confirmed the values obtained by the thiocyanometric method. Criticism was also made of Cocchinaras' attempt[13] to analyse linseed oil by a bromination method followed by analysis of the resultant bromo-acids, and the findings of the present investigation support the contention that his results are based on an untenable assumption.

Davidsohn[14] observed that oils obtained from linseed and sunflower seed that have ripened in cold climates have a higher iodine value—and presumably a higher linolenic and linolic acid content—than oils obtained from similar seed grown in hotter climates where conditions apparently favour the production of oleic acid. Apart from this statement, and that of Griffiths and Hilditch (*loc. cit.*) that it seems almost certain that Argentine (Plate) and also Calcutta linseed oils contain a mixture of fatty acids consisting within approximate limits of about 10 per cent. of saturated, about 10 per cent. of oleic, about 40 per cent. of linolic and about 40 per cent. of linolenic acid, no record appears to have been made of any effort to determine and compare the compositions of linseed oils of varying origin.

With the aim of correcting this omission, typical samples of Baltic, Indigene, Calcutta and Plate linseed oils have now been analysed by methods of analysis proved to be capable of giving accurate and repeatable results.

The samples of raw linseed oil chosen for examination were known from previous experience to be truly representative of their type; the actual samples were withdrawn from new bulk supplies, and in each instance analysis was completed within two months of the date of crushing.

Particulars of the samples investigated are as follows:—Indigene oil (I), received February, 1935; Baltic oil (B), received March, 1934; Plate oil (P), received May, 1934; Calcutta oil (C), received July, 1934.

The seed from which the oil was expressed by the crushers was from the previous year's crop in each instance.

In addition to the above-mentioned samples of new oil, a sample of raw Baltic oil (BB) received and originally analysed in February, 1909, and subsequently stored in a sealed bottle full to the neck and kept in the dark, has been examined. This oil is very viscous and red in colour; it has a distinctive and fatty odour but is perfectly clear and free from "break." The oil when originally examined in 1909[15] had the following characteristics: Sp.gr. at 15·5° C, 0·9357; n_D^{20} 1·4840;

iodine value (Wijs method; 2 hours' contact), 198·5; saponification value, 185; free fatty acid content, 1·25 per cent.

EXPERIMENTAL.—The methods employed during the investigation were those generally accepted and are outlined below.

The refractive index was determined by means of an Abbé refractometer, the free fatty acid content was expressed in terms of oleic acid, the saponification value was determined by heating for 45 minutes under reflux with alcoholic potash, and the Wijs method was used for determining the iodine value, a two hours' contact period being allowed.

The thiocyanogen value was determined by the modification of Kaufmann's original method outlined by Griffiths and Hilditch (*loc. cit.*), and the results obtained both on the oil and on the constituent fatty acids fully confirm the statement of Griffiths and Hilditch that, provided great care is taken to keep all reagents absolutely dry, results agreeing well with each other may be obtained at any time.

TABLE III

	Indigene oil (I.)	Baltic oil (B.)	Calcutta oil (C.)	Plate oil (P.)	Baltic oil (BB.)
Raw oil					
Sp.gr. at 15·5° C.	0·9344	0·9347	0·9321	0·9323	0·9890
n_D^{20} ..	1·4800	1·4825	1·4808	1·4757	1·4875
Free fatty acid, per cent.	3·05	1·25	0·80	0·80	20·1
Sapon. value ..	190·0	189·0	190·3	190·2	206·4
Iodine value ..	189·1; 189·8	195·3	182·4	180·7	148·1; 147·2; 146·3
Thiocyanogen value	118·9; 119·2; 119·0	115·0; 113·4; 115·9	112·3; 111·4; 115·1	114·3; 115·0; 115·7	89·4
Unsaponifiable matter, per cent. ..	1·24	1·26	0·73	0·78	0·72
Fatty acids, per cent.	94·6	94·6	94·9	94·8	92·8
Fatty acids					
Equiv. weight	294·0	290·8	288·0	284·1	297·8
Iodine value	197·9; 198·2	203·4	191·6; 190·9	187·1; 186·4; 188·9	161·6; 162·2; 161·9
Thiocyanogen value	121·9; 122·1	126·5; 125·8; 126·8; 126·3	121·2; 120·1	119·8; 118·9	98·7
Constituents, per cent.:					
Saturated (*a*) (found)		5·3 } 6.6	7·8 }	8·2 } 9·7	26·4 20·2 18·2
(*b*) (found)	11·6 11·1	7·9	10·8	11·3	10·7 10·8
Oleic (calc.)	6·1	9·3	13·7	17·4	—
Linolic (calc.)	37·4	39·5	36·7	33·4	—
Linolenic (calc.)	45·2	44·1	40·3	39·5	

(*a*) Estimated by the lead salt and ether method.
(*b*) Estimated by Bertram's oxidation method.

The linseed oil mixed fatty acids were obtained by saponifying the oil (5 g.) by heating under reflux with aqueous potassium hydroxide (4 g. in the minimum amount of water) and rectified spirits (30 ml.) for 20 minutes, removing the solvent by distillation *in vacuo* over a boiling water-bath, dissolving the soap thus obtained in warm water (200 ml.), liberating the acids by addition of a few ml. of conc.

sulphuric acid, taking them up in ether, and washing the ethereal solution with water. After immediate evaporation of the solvent, the residual fatty acids were kept at 100° C. for one hour under reduced pressure, a capillary leak fed by coal gas being used throughout. The iodine and thiocyanogen values were then determined immediately, the bulk of the fatty acids being weighed prior to their addition dropwise to the reagent, and the amount added being found by difference. This was found to be a necessary precaution, as otherwise rapid oxidation was liable to occur, resulting in values appreciably lower than those obtained when this precaution was observed.

The estimation of the saturated acid content of the mixed fatty acids was made both by the lead salt and ether method[16] and by Bertram's oxidation method,[17] the precautions indicated by Hilditch and Priestman[18] and by Gay (*loc. cit.*) being observed in making the latter estimation. For the purposes of the later calculations the mean of the results obtained by the two methods has been taken as the saturated acid content.

The experimental results are recorded in Table III (p. 267).

From the results in that table, the constitution of the new oils has been calculated, use being made of the fact observed by Kaufmann (*loc. cit.*) that only two of the double bonds in linolenic acid and one double bond in linolic acid are reactive towards free thiocyanogen. This reasoning is applicable only when the mixed fatty acids are composed of individuals capable of reacting with thiocyanogen in a known manner, and in consequence cannot be applied to sample (BB), which has obviously undergone both oxidation and polymerisation during its twenty-six years of storage, with consequent formation of a complex the reaction of which with free thiocyanogen is uncertain.

The calculated composition of the four new oils is recorded in Table IV.

TABLE IV

	Fatty acids, per cent.				Glyceryl radicle Per Cent.	Unsapon. matter Per Cent.
	Saturated	Oleic	Linolic	Linolenic		
Indigene oil (I) ..	10·7	5·8	35·4	42·7	4·2	1·2
Baltic oil (B) ..	6·2	8·8	37·4	41·8	4·1	1·3
Calcutta oil (C) ..	8·8	13·0	34·9	38·3	4·4	0·7
Plate oil (P)	9·2	16·5	31·7	37·4	4·4	0·8

DISCUSSION OF RESULTS.—An examination of the results recorded in Tables II and IV shows that the composition of the mixed fatty acids obtained from Calcutta and Plate linseed oils from widely differing sources is fairly constant. The compositions of six out of the seven samples in question are comparable and fall within the following narrow limits: saturated acids, 8·5 to 11·3; oleic acid, 8·0 to 17·4; linolic acid, 33·4 to 42·6; linolenic acid, 36·3 to 42·1 per cent. The recorded composition of the seventh—that of Eibner and Brosel—can hardly be correct, as the iodine value of a mixture of the type indicated would be 193—a value far in excess of that normally obtained for an average oil of this type.

Comparison of the composition of the mixed acids obtained from sample (B), with the average composition of Calcutta and Plate oil acids, shows definitely that the markedly superior drying and heat-polymerising properties of the Baltic type of oil are due to its containing a high percentage of the most highly unsaturated acids.

The results obtained from the examination of the sample (BB) of old Baltic oil, are of little immediate value; it had been hoped to examine this oil in more detail, but as the investigation had to be discontinued at this stage it was thought advisable to publish the results already obtained.

Sufficient has been done, however, to show that, on standing, a linseed oil of this type develops an appreciable free acidity—which accounts for the observed increase in the saponification value—and that considerable saturation of the double bonds takes place. It is also safe to assume from the experimental findings and from the excessive increase in viscosity observed, that polymerisation, rather than oxidation, is the principal cause of the apparent saturation. The saturated acid content of this old oil is very little, if any, greater than normal when determined by Bertram's oxidation method, from which it is apparent that the partially saturated oil on saponification affords acid products which are capable of fission by alkaline permanganate in a normal manner. The uncertainty of the lead salt method shows that, in addition to lead palmitate and lead stearate, acids are produced which give lead salts that are insoluble in ether. The equivalent weight of these acids is slightly higher than usual, but the observed values may be low, as it is possible that a certain amount of depolymerisation occurs during alcoholic saponification.

My thanks are due to the Directors of Messrs. Jas. Williamson & Son, Ltd., Lancaster, for permission to publish this paper, to Mr. Rowland Williams for his continued interest in the investigation, and to Mr. T. Newton for his assistance in carrying out some of the analytical work.

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RESEARCH DEPARTMENT
JAMES WILLIAMSON & SON, LTD.
LANCASTER

December 24th, 1938

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SPIRIT VINEGAR CONTAINING MALT VINEGAR

The analysis of a recent sample of "English Spirit Vinegar" may be of interest, since it is the only time to my knowledge that the presence of malt vinegar in spirit vinegar has been recorded.

The oxidation, iodine and ester values were determined by the methods proposed by Edwards and Nanji (Analyst, 1938, **63**, 410) and were proved to be of considerable value in ascertaining the nature of the mixture.

For purposes of comparison the average percentage figures obtained with malt vinegars (61 samples) and spirit vinegars (*loc. cit.*) are given below with the range of oxidation values, etc., and also the results obtained with the sample.

	Malt vinegar	Spirit vinegar	Mixture 40 : 60	Sample	Caramel solution of equal colour
Total soluble solids, per cent.	2·16	0·23	1·00	1·23	0·30
Ash, per cent.	0·25	0·06	0·136	0·123	0·023
Nitrogen, per cent.	0·075	0·035	0·051	0·045	0·0054
Phosphoric anhydride, per cent.	0·070	0·025	0·043	0·044	0·000
Oxidation value	552–1320	88–225	274–663	625	1·4
Iodine value	688–1976	8–27	280–806	347	1·5
Ester value	29–66	6–14	15–35	67	1·2
Acetic acid	—	—	—	4·6	—

It was reported that the analysis indicated the presence of 40 per cent. of malt vinegar, with an observation that such admixture might render the article unsuitable for some of the purposes for which spirit vinegar is used.

The manufacturers of the vinegar were asked for an explanation; in reply, they denied that any malt vinegar was added to their spirit vinegar, and suggested that the soluble matter found on analysis might be derived from the caramel that is added to colour the spirit vinegar (to meet the public demand).

In the analysis, however, due consideration had already been given to the effect of the added caramel; an aqueous solution made from a sample of commercial caramel, as sold for colouring purposes, and diluted so as to contain the same percentage of total soluble solids as the vinegar, *i.e.* 1·23 per cent., was found to be four times as dark as the vinegar. This solution was diluted until its colour was equal to that of the vinegar and then analysed: the figures obtained are given in the fifth column above, and it may be seen from these results that the addition of such caramel could have had no appreciable effect on the phosphorus, oxidation, iodine and ester figures.

At a subsequent interview a director of the company manufacturing the vinegar stated that they had themselves since had bottles of the vinegar returned by a customer who had noticed a difference in the quality, and that on further investigation they had found that the samples did contain at least 40 per cent. of malt vinegar. The trouble arose in the pasteurising plant through a shop steward misunderstanding his instructions. He had always emptied the pasteuriser when switching over from spirit to malt vinegar but not when changing from malt to spirit, under the impression that it could not matter if a customer got some of the better article. This meant in practice that when the switch-over occurred some dozens of bottles were filled with a mixture of malt and spirit vinegar, in gradually decreasing quantities of malt.

Malt vinegar is dearer than spirit vinegar, and the director expressed his regrets for the admixture and his gratitude for having had his attention drawn to a matter which meant a loss to his firm as well as possible loss of the custom of those manufacturers and retailers who might find the mixture unsuited to their particular needs.

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THE DETECTION OF ZINC IN PRESENCE OF IRON

IT is well known that zinc in a solution containing hydrochloric acid gives with an alkali ferrocyanide a white precipitate of potassium zinc ferrocyanide of uncertain composition. The reaction is probably $2Fe(CN)_6'''' + 2K^{\cdot} + 3Zn^{\cdot\cdot} = Zn_3K_2[Fe(CN)_6]_2$ (*cf. Treadwell's Analytische Chemie*, Vol. I, p. 184, 1935 edition, Zurich).

This test, first applied by Galetti, cannot be used when iron is present, because then Prussian blue masks the precipitate of the zinc complex. To prevent this, the test may be modified by adding an alkali fluoride, which eliminates the iron ions in the form of a complex: $Fe^{\cdot\cdot\cdot} + 6F' = FeF_6'''$. This iron fluorine complex is soluble and in such a solution there are too few iron ions to form Prussian blue. There is no interference, however, with the zinc ions, so that the reaction may be used in qualitative analysis.

The procedure is as follows:—The solution under examination is treated with 0·5 to 1 ml. of 2 *N* hydrochloric acid and with sufficient alkali fluoride to cause decolorisation; according to the equation above the quantity of fluoride required depends on the quantity of iron ions present. To ascertain if enough fluoride has been added, a drop of the solution is applied to ferrocyanide paper; if the paper turns blue, there is insufficient fluoride. The mixture is filtered into another test-tube, the first tube and the funnel are washed with 1 to 2 ml. of water, and the washings are added to the filtrate. As thus obtained the solution is perfectly clear and gives with 1 to 3 ml. of potassium ferrocyanide solution a white amorphous precipitate. With a low concentration of zinc ions the precipitate is obtained 2 or 3 minutes later. The test must be made at the ordinary temperature; the solution must not be warmed because the acid then decomposes the ferrocyanide. The test is capable of detecting $0{\cdot}1\gamma$ of zinc; the limit of dilution is 1 : 500,000. If the precipitate shows any trace of colour, too little fluoride has been used, and the test must be repeated after addition of more.

Numerous experiments have proved that potassium ferricyanide gives still better results than ferrocyanide. The precipitate is then of slightly brown tint. Although the degree of sensitivity is essentially the same as with ferrocyanide, the precipitate appears sooner and it is more easily seen. The composition of the precipitate is uncertain.

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TURMERIC TEST-PAPERS CONTAINING BORON

IN view of the extensive use of turmeric papers in qualitative tests for boric acid and borax, it was thought that a recent experience of mine would be of interest. It was found that books of turmeric papers supplied by a well-known firm gave a strongly positive reaction even when the solution under test was known to be free from boron compounds. So pronounced was the reaction that it was concluded that the papers themselves contained boron in some form, and this fact was established by ashing several papers and obtaining methyl borate from the ash. On taking up the matter with the suppliers, their chemist was able to confirm the presence of boron in the papers. An apology was sent but no explanation of how the boron came to be present was forthcoming. It should be mentioned that these faulty test-papers were quite normal in appearance, and as such an occurrence does not appear to have been noticed before, it was considered desirable to place it on record.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1938

OF the 1402 samples submitted under the Food and Drugs Act, 26 were bought formally.

CARBOLIC ACID OINTMENT.—According to the B.P. this ointment is made by dissolving 30 g. of phenol in a mixture of 75 g. of beeswax, 50 g. of lard, and 845 g. of hard and soft paraffins, so that theoretically the finished article should contain 3·0 per cent. of phenol. It was mentioned in a paper read before the Pharmaceutical Conference in September, 1938, that if the temperature of the melted base is 60° C. amounts of phenol, ranging in test experiments from 3·7 to 5·2 per cent., are lost during the manufacture, *i.e.* the ointment should contain about 2·9 per cent. of phenol. Of 10 samples analysed, only 2 were in reasonable agreement with this figure, containing 2·9 and 2·7 per cent. respectively. Three others contained 2·1, 2·3 and 2·3 per cent. and, having regard to the difficulties in the process of manufacture, were passed as genuine. It was also stated in the above-mentioned paper that if the ointment is stored in pots with loosely fitting earthenware covers, phenol is rapidly lost; in one instance the loss amounted to 11·2 per cent. in 10 months and to 28·2 per cent. in 25 months. Under warmer conditions the loss reached 35 per cent. in 25 months. A sample kept at room temperature in a 2-oz. pot covered with grease-proof paper lost 28 per cent. from the top layer in 5 months as compared with 7·1 per cent. from the whole (mixed) sample. Samples of ointment bought from retail pharmacists contained from 0·5 to 2·7 per cent. of phenol. One of the samples examined in the Birmingham laboratory was in a cardboard container in the pattern of a chip-box; it contained only 1·8 per cent. of phenol. The stock was withdrawn from sale. A sample taken from a 1-oz. tin at the same shop contained 2·55 per cent. of phenol. Another of the 10 samples contained 1·9 per cent. of phenol and was sold from a 1-lb. jar purchased at the end of 1937. Two further samples from different retailers, but both bought from the same wholesale firm, contained only 1·3 and 1·2 per cent. of phenol respectively. The former had been supplied in March, 1936, and the latter in March, 1935. Both retailers were advised to purchase the ointment in the smallest possible quantities, or at least in small containers so as to reduce to a minimum the tendency to loss of phenol.

H. H. BAGNALL

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1938

OF the 770 samples taken under the Food and Drugs Act, 47 were purchased informally.

Under the Fertilisers and Feeding Stuffs Act, 1926, the inspectors took 38 samples on the premises of sellers, and the official samplers took 89 samples formally at farms on behalf of farmers. Also, at the request of farmers 114 samples were taken informally, and purchasers sent 63 samples direct to the laboratory.

WHITE FISH MEAL.—A sample warranted to contain 5 per cent. of oil was found to contain 6 per cent. As the Fertilisers and Feeding Stuffs Act permits this product to contain 6 per cent. of oil but no more, the sample in question could be deemed to consist of "white fish meal," although its oil-content exceeded the warranty. A low oil warranty helps to sell a fish meal, and it is therefore important to see that the warranties given are complied with; there is a tendency for feeding fish meals to contain more than the permissible amount of oil.

WET SHODDY.—Of 68 samples of shoddy sold with a warranty, 35 were deficient in nitrogen. The largest deficiences were found in the following samples:

Water Per Cent.	Mineral matter Per Cent.	Nitrogen guaranteed Per Cent.	Nitrogen found Per Cent.	Nitrogen deficiency Per Cent.
39·0	11·6	5·76	3·06	2·70
45·0	12·2	5·76	2·89	2·87
37·0	11·8	5·76	3·38	2·38
38·0	15·6	5·76	3·49	2·27
39·0	9·4	5·76	3·67	2·09

These results show that the deficiencies occurred in one class of shoddy and that these shoddies contained excessive amounts of water. The mineral matter, too, was somewhat high. Nitrogen deficiencies exceeded 1 per cent. in 20 of the shoddies. For some years past few wet shoddies have been encountered, and it was assumed that greater care was being taken by shoddy merchants to protect shoddy from the weather. From the condition of some of the samples examined during the last few months it can be definitely stated that there are some merchants who have taken no trouble to prevent undue exposure. In any event, it is difficult to understand the conditions under which shoddy containing 45 per cent. of water could have been stored, for it would mean that on every ton of shoddy nearly one ton of rain fell and was absorbed. Before the days of the sale of shoddy at "unit value" it is alleged that it was a common practice to play a hose-pipe upon a bulk of shoddy before consigning it to a farmer. As a large proportion of the shoddy bought in the county is not examined, it would probably still pay an unprincipled merchant to take no precautions to prevent shoddy from becoming wet.

BAT GUANO.—A considerable quantity of this material, deposited by bats in caves years ago, was offered for sale. It was a dark brown powder containing 12 per cent. of nitrogen, 8 per cent. of phosphoric acid and 4 per cent. of potash.

F. W. F. ARNAUD

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

DERMATITIS FROM WEARING APPAREL

GRIFFITHS *v.* PETER CONWAY, LTD.

ON February 28th the Court of Appeal dismissed, with costs, an appeal by the plaintiff from the judgment of Mr. Justice Branson in a case heard at the Bristol Summer Assizes on July 6th and 7th, 1938, in the High Court of Justice, King's Bench Division.

In June, 1937, the plaintiff bought from the defendants, who are retail tailors, a Harris tweed coat, which was specially made for her. She contracted dermatitis shortly after beginning to wear it and brought an action to recover damages for breach of warranty. Mr. Justice Branson held that the real cause of the trouble was that the plaintiff's skin was not normal, but had an idiosyncratic effect, so that what the plaintiff contracted was idiosyncratic dermatitis, a thing which no purveyor of cloth could really guard against to any further extent than purveyors of cloth have guarded against there being anything harmful in its texture.

The plaintiff relied upon the fact that she had made known to the defendants the particular purpose for which the goods were required, *i.e.* for her own use, and her counsel (Mr. Morris) contended that this brought the case within the exception to Sec. 14, Sub-sec. (1) of the Sale of Goods Act, 1893. This section negatives any implied warranty or condition as to the quality or fitness for any particular purpose of goods supplied under a contract of sale except "where a buyer expressly, or by implication, makes known to the seller the particular purpose for which the goods are required, so as to show that the buyer relies on the seller's skill or judgment, and the goods are of a description which it is of the seller's business to supply (whether he be the manufacturer or not), there is an implied condition that the goods shall be reasonably fit for such a purpose."

The Master of the Rolls, dealing with the argument that Mrs. Griffiths had expressly made known to the defendants the particular purpose for which the goods were required, said that there was one quite sufficient answer to the argument. Before the condition was implied as to reasonable fitness, it was necessary that the buyer should make known, expressly or by implication, first of all, the particular purpose for which the goods were required. The particular purpose for which the goods were required was for the purpose of being worn by a lady suffering from an abnormality. It seemed to him (the Master of the Rolls) that if a person suffering from such an abnormality desired an article of clothing for his or her use, and desired to obtain the benefit of the implied condition, he or she did not make known to the seller the particular purpose merely by saying "the article of clothing is for my own wear."

The essential matter for the seller to know in such cases with regard to the purpose for which the article was required consisted in the particular abnormality or idiosyncrasy from which the buyer suffered. It was only when he had that knowledge that he was in a position to exercise his skill or judgment. The fact that those essential characteristics were not made known, and indeed were not known, as in the present case they were not known, to the buyer, did not seem to affect the question. When he spoke of "essential characteristics" he was not, of course, referring to variations which took place and existed within the class of normal people. No two normal people were precisely alike, and in the matter of sensitiveness of people who would be described as normal, their sensitiveness must vary in degree. But there was a line which it was no function of any Court, or indeed of any medical man, to draw with preciseness so as to cover all cases where normality ceased and abnormality began. It was a question that no judge and no jury would have any real difficulty in deciding on the evidence in any particular case. In this particular case the learned Judge had found the existence of abnormality, and that being so, it seemed impossible to say that the seller here had the particular purpose pointed out to him so as to show that the buyer relied on his skill and judgment.

Lord Justice Mackinnon and Lord Justice Goddard, who sat with the Master of the Rolls, concurred with the decision.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1937–1938*

As Professor Fowler was unable, for reasons of health, to take office as Director of the National Physical Laboratory, the Committee of the Privy Council appointed Dr. C. G. Darwin, M.C., Sc.D., F.R.S., Master of Christ's College, Cambridge, to be Director. Until Dr. Darwin entered upon his duties on December 1st, 1938, Sir Frank Smith, the Secretary of the Department, was appointed to hold the office of Director.

The gross expenditure of the Department last financial year was £872,127, and the receipts from industry and other sources were nearly £235,000.

The Report makes the usual survey of the activities of the Department, and gives an account of some of the many problems the solution of which is being sought through the co-operation of science and industry.

FOOD INVESTIGATION.—Special attention is called to the results achieved under the Department's Food Investigation Board in the last few years, and particularly in the development of gas-storage. "Ten years ago there were no gas stores. To-day they provide three million feet of storage, and this is only a beginning."

Up to 1933 Australia and New Zealand could send us only frozen beef, but as a result of the Department's work it has been shown that chilled beef can be preserved for sufficiently long periods in special chambers containing carbon dioxide. This discovery has been rapidly developed commercially, and in 1937 Australia and New Zealand sent to this country about 750,000 cwt. of chilled beef carried in this way.

The Food Investigation Board is to be invited to review the whole field of research into the processing of foodstuffs and to submit proposals for embracing under their scientific supervision such work as they may consider to be desirable in the national interest.

GRAIN AND INSECTS.—Another new field of investigation to be undertaken by the Department is the study of the attack on grain by insects. It has been estimated that the destruction of grain by weevils and other pests in this country represents, on a conservative estimate, a loss of over £500,000 a year. The industrial interests concerned have, as a start, contributed £1200 to enable a complete survey of the problem to be made as a first stage in the initiation of research to solve it.

NUTRITIVE VALUE OF BREAD.—The results of investigations have emphasised the importance of bread and butter in the dietary. It has been shown that certain fats, such as lard or butter, reduce the effects of calcium deficiency in the diet, presumably by rendering the actual calcium-content of the food more completely assimilable. "At the same time it is well known," the report states, "that fat is not completely assimilated by the body except when eaten with a relatively large excess of carbohydrate such as bread or potatoes."

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* H.M. Stationery Office, York House, London, W.C.2. Cmd. 5927. Price 3s. net.

For Report of the Building Research Board see ANALYST, 1938, **63**, 499; Atmospheric Pollution Committee, *id.*, 1938, **63**, 340; Food Investigation Board, *id.*, 1938, **63**, 818; Forest Products Research Board, *id.*, 1938, **63**, 46, 430; Chemistry Research Board, *id.*, 1939, **64**, 35.

RESEARCH ASSOCIATIONS.—The development of co-operative research is strikingly illustrated by figures given in the Report. These show that over a period of ten years the annual amount subscribed by industry for such co-operative research has more than doubled, having increased from just over £120,000 in 1929 to about £265,000 in 1937. Work is now being carried out in more than twenty Research Associations with the assistance of grants from the Department. The two largest are the Cotton Research Association and the Electrical Research Association. The former has now an income of over £87,000 and the latter an income of over £85,000 a year.

During the year a new Research Association was formed. This is the British Coal Utilisation Research Association which has taken over the activities of the Research Department of the Combustion Appliance Makers' Association and is to develop research on the general problem of the utilisation of coal. As a result of the offers of grant assistance made by the Department, the Association will have a minimum income of £18,000 a year with a prospect of an annual income of £30,000 if full advantage is taken of the offer made.

Among the points of interest in the work of the Research Associations the Report directs special attention to the following:

POWDERED RUBBER.—A simple process has been devised by the Rubber Research Association for preparing powdered rubber from the ordinary dry rubber of commerce.

MEASUREMENT OF THE TEMPERATURE OF LIQUID STEEL.—The National Physical Laboratory is co-operating with the Iron and Steel Industrial Research Council and the Iron and Steel Institute in investigating methods for measuring the temperature of liquid steel in open hearth furnaces. The aim is to attempt to adapt the platinum thermo-couple and the optical pyrometer to the conditions of the open hearth furnaces. Refractory materials have been found which will afford adequate protection to the measuring instruments when immersed for short periods in molten steel without slag, and in the next stage of the investigation an attempt is being made to obtain such slag-free conditions in an actual furnace as will enable the "quick-immersion" method to be brought into use.

DETERIORATION OF BRICKS IN BLAST FURNACES.—Under the Refractories Research Association, investigations have been made on bricks taken from the linings of blast furnaces. The deterioration occurring at different zones of a furnace due to the action of carbon monoxide, alkali salts, zinc and lead compounds, etc., has been examined. The results have indicated methods for producing fire bricks which are resistant to the action of carbon monoxide. Suggestions have also been made regarding the composition of cements for joints between bricks in the various zones.

CAST IRON WITH INCREASED TENSILE STRENGTH.—The Cast Iron Research Association has now produced cast iron having a tensile strength of 60 tons per sq. in. A few years ago it was not possible to obtain a strength of more than about 12 tons per sq. in. Tests have been carried out at the National Physical Laboratory on crank-shafts cast from materials supplied by the Research Association. Aluminium cast iron shows particular promise as a heat-resisting material.

NON-SHRINKABLE WOOL.—Commercial working has begun on the Wool Industries Research Association's chlorination process for the production of wool resistant to shrinkage, and the trade mark "Woolindras" has been registered to protect the new standard of unshrinkability attainable in woollen goods placed on the market.

An entirely new method of producing non-shrinkable wool is under investigation. In this process use is made of certain proteolytic enzymes. One type suitable for the process is papain. The activity of the enzymes can be controlled chemically, and they appear to have a specific action on certain regions of the wool fibre. It is too early to speak of the special advantages of this new type of treatment.

RUBBERISED WOOL.—The development of the process for the rubberisation of wool has been continued, and quantities of various types of wool yarn have been treated for members of the Association in order to test the properties of fabrics made from wool. The treatment has proved advantageous for various types of woven and knitted fabrics in which resistance to wear or avoidance of the objectionable "balling-up" which may result on wearing surfaces of garments made from loosely-twisted yarns are matters of importance. The resistance of carpets to wear also appears to be greatly improved.

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY

III. SULPHUR DIOXIDE*

THE third of the leaflets describing standard methods for the detection of toxic gases in industry (*cf.* ANALYST, 1937, **62**, 607; 1938, **63**, 658) deals with sulphur dioxide. It is pointed out that the situations where this gas may be encountered in possibly dangerous concentrations include bone and glue works, cold storage and refrigeration plant, dye-making, dyeing and bleaching works, glass and pottery works, ore roasting (metallurgical) works, petroleum refining works, rubber works, sulphuric acid works and tanneries. It is also encountered in fumigation and disinfection.

POISONOUS EFFECTS.—Sulphur dioxide in high concentrations is irrespirable and causes asphyxiation. In lower concentrations it is irritating to the eyes, nose, throat and lungs. It may also cause inflammation of the nose and throat and set up bronchitis from prolonged exposure to relatively low concentrations which, since they cause no immediate or marked discomfort, can be tolerated for a considerable time. The following figures (Henderson and Haggard, *Noxious Gases*, 1937) show the approximate concentrations that are permissible:

Parts per vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 100,000	0·03	Maximum concentration allowable for several hours' exposure.
1 in 2000	1·4	Concentration dangerous even for short exposures.

METHODS OF DETECTION.—The potassium chromate test is considerably less sensitive than the potassium ferricyanide and ferric chloride test or than the starch iodate test, and is not capable of detecting sulphur dioxide in concentrations such as are met with in the atmosphere of works. Potassium ferricyanide and ferric chloride test-paper is sufficiently sensitive, but readily becomes coloured when kept, and the test is therefore unsuitable for standardisation on a quantitative basis. For these reasons a test based on the use of starch—potassium iodate—potassium iodide—glycerol test-paper has been adopted as the standard method. By drawing the air *through* the test-paper (*cf.* Leaflet No. 1; ANALYST, 1937, **62**, 607) concentrations down to 1 part in 250,000 (0·0114 mg. per litre) can be estimated by making not more than ten strokes with a hand-pump. As the test is not specific for sulphur dioxide, it is necessary, when the presence of other gases which would affect the test is suspected, to identify these gases and interpose a suitable trap for them.

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* Leaflet No. 3. H.M. Stationery Office, York House, Kingsway, London, W.C.2. March 7, 1939. Price 2s. 6d. net.

DETAILS OF THE TEST.—Samples shall be taken at a point closely adjacent to the workers. In testing the atmosphere of a tank, prior to the entry of a workman, it may be necessary to take samples at intervals throughout the period of work.

Apparatus.—The hand-pump and the technique of sampling the atmosphere are as described in Leaflets Nos. 1 and 2 (ANALYST, *loc. cit.*).

Test-papers.—Twelve ml. of approx. $N/10$ barium hydroxide solution are added to 60 ml. of water. One g. of Lintner's soluble starch (of reagent quality) is made into a thin cream with about 10 ml. of the water so treated, and the remainer is boiled. To the boiling liquid are added 1 g. of potassium iodate and 2 g. of potassium iodide (both of reagent quality); when these are completely dissolved the starch cream is added and boiling is continued for a few minutes, after which the solution is cooled, 30 ml. of pure glycerol are added, and the mixture is thoroughly shaken and made up to 100 ml. with water. As thus prepared the reagent should have a *p*H of approximately 9·5.

The test-papers are prepared from Postlip No. 633 extra-thick white filter-paper (18 × 24; 60 lb.) cut into strips 2 in. wide. The strips are immersed for 30 seconds in the reagent, the excess of liquid is drained off, and the strips are pressed two or three times between dry filter-paper, and suspended for 10 minutes at 50° C. in a well-ventilated oven free from acid fumes. One inch at the top and bottom of each strip is cut off and discarded, and the remainder is cut into 3-in. lengths for use. The test-papers should preferably be used within a few hours after preparation; they may, however, be stored in a well-stoppered bottle in the dark, and used after 1 or 2 days if discoloration is not serious. The reagent may be used up to 7 days after preparation.

Method.—The test-paper is inserted in a special holder and the test is applied by a technique similar to that already described in Leaflets Nos. 1 and 2 (*loc. cit.*). Any stain obtained is compared immediately with the standard chart provided with the Leaflet; or, alternatively, other methods of comparing the colours may be used, such as a comparator using coloured glasses as a standard, a photo-electric colorimeter or an optical density meter, provided that the standards have been properly calibrated and are used according to standard instructions.

Methods of applying the test to air from a space which is not readily accessible are described.

FIRST AID.—Full details of the treatment of cases of gassing are given in Factory Form No. 395 (H.M. Stationery Office, price 1d. net).

IV. BENZENE VAPOUR*

BENZENE vapour is produced during the manufacture of coal gas and the distillation of coal tar. It may be encountered in dangerous concentrations in many industrial situations including aeroplane works, cellulose paint, lacquer and leather cloth works, dyestuffs and intermediate works, explosives works, fat and glue works, gas works and coke ovens, linoleum works, motor fuel blending works, paint and varnish works, pharmaceutical and perfumery works, rubber works, spray-painting works, and tar-distilling works.

POISONOUS EFFECTS.—In high concentrations benzene vapour acts as a narcotic (acute poisoning). In low concentrations over a prolonged period it affects the blood and the blood-forming organs of the body (chronic poisoning). Individual susceptibility is well recognised, women and young persons being particularly liable to suffer from chronic poisoning.

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* Leaflet No. 4. H.M. Stationery Office. March 7th, 1939. Price 3d. net.

The following figures, based on Henderson and Haggard (*Noxious Gases*, 1927), show the effects of exposure to various concentrations:

Parts per vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 700 to 1 in 300	5 to 11	Slight symptoms after several hours' exposure.
1 in 300 to 1 in 200	11 to 17	Max. concentration that can be inhaled for 1 hour without serious disturbance.
1 in 140	26	Serious illness after 30 to 60 minutes' exposure.
1 in 50	70	Rapidly fatal.

Analyses of air in factories where poisoning has occurred gave values ranging from 1 in 200 to 1 in 500 parts.

Owing to its low solubility in the blood, most of the benzene absorbed is eliminated through the lungs; from 15 to 30 per cent., however, is oxidised in the system and eliminated through the kidneys—a slow elimination which favours cumulative effect on repeated exposures.

In acute poisoning the symptoms in slight cases are giddiness and a state of excitement. If the vapour is inhaled in quantity, coma quickly follows. The skin becomes somewhat livid and convulsions or twitchings of the muscles are noticeable.

In chronic cases there is aplastic anaemia. The number of red corpuscles is reduced and there is first an increase and then a reduction in the number of white cells. Bleeding from the mucous membrane of the mouth is one of the earliest manifestations. Later, haemorrhages occur under the skin, and severe bleeding from the mucous haemorrhages is frequently the cause of death. This form of anaemia is usually fatal, and even when recovery takes place, convalescence is very slow.

METHODS OF DETECTION.—More than 1 mg. per litre of air (about 1 in 3500) must be present before the odour of benzene can be distinctly perceived. Most of the chemical methods of detection involve nitration to nitrobenzene with subsequent conversion into compounds that can be estimated colorimetrically. These are too long and complicated to be suitable as standard tests in industry. A more simple test has, however, been developed, involving the absorption of the vapour in conc. sulphuric acid containing a trace of formaldehyde; an orange-brown colour is produced even by traces of benzene (down to 1 part in 10,000).

The test is carried out by drawing a sample of the atmosphere under test through a tube containing the reagent by means of a hand-pump of definite capacity, and determining the number of strokes required to produce a certain standard depth of colour. From the number of strokes of the pump required to produce the standard colour, the concentration of benzene vapour present is obtained by reference to the table given in the detailed instructions in the Leaflet.

The test is slightly more sensitive to toluene than to benzene, but, since both vapours have roughly the same toxicity, no distinction between them will normally be necessary.

With solvent naphthas (xylenes and their higher homologues) little more than a qualitative indication would be given by the test. Naphthalene vapour interferes by producing a black film on the reagent. Vapours of crude benzoles may contain compounds, such as thiophen, which interfere with the test by imparting a yellow or red colour to the sulphuric acid. Their presence may be detected by pumping the air sample through a bubbler of conc. sulphuric acid alone, when the respective colour only will be produced. Usually, however, the quantities of such substance in commercial grades of benzole are insufficient to affect the test.

DETAILS OF THE TEST.—The method of sampling the atmosphere by means of a hand-pump is the same as previously described (Leaflets Nos. 1 and 2, *loc. cit.*). The sample is drawn through the reagent contained in a bubbler consisting of a side-arm test-tube of approx. 0·75 in. internal diameter and about 6 in. long, fitted with a rubber bung through which passes a delivery tube (approx. 0·125 in. bore) reaching nearly to the bottom of the test-tube and terminating in a fine jet. The bubbler is mounted on the barrel of the pump in such a way that the reagent can be easily seen and the tube readily removed for comparison with the standard and replacement by a fresh tube. A trap is inserted between the pump and the bubbler to prevent the reagent being drawn into the pump.

A convenient arrangement of the apparatus is described and illustrated in the Leaflet.

Preparation of Reagent.—The measured quantity (0·5 ml.) of 40 per cent. formaldehyde is introduced into the bubbler by means of a graduated pipette, the volume is made up to 10 ml. with conc. sulphuric acid, and the mixture is well stirred.

Preparation of Standard Colour.—One g. of sodium nitroprusside (of analytical reagent quality) is dissolved in 100 ml. of water. If kept in the dark in a well-stoppered flask, the solution should not deteriorate in 2 weeks. A slight alteration in shade, but not in depth of colour, may occur; if this becomes marked, a fresh solution must be made up.

Method.—The pumping with the hand-pump must be continued until the depth of colour developed is approximately that of the standard colour (the number of strokes made being counted). The bubbler is then removed and immediately compared, side by side, with the standard tube, in daylight reflected from a white surface held 2 to 3 in. behind them. If the colour of the test sample is less than that of the standard, the bubbler is replaced and further strokes of the pump are made until equivalence is reached; if the test colour is the deeper the test must be repeated with a fresh tube of reagent.

The following table gives the number of strokes necessary for various ranges of concentration in order to obtain the standard colour:

Concentration	Number of strokes
Up to 1 in 700	Less than 1
1 in 700 to 1 in 1200	1 to 2
1 in 1200 to 1 in 1500	2
1 in 1500 to 1 in 2000	3
1 in 2000 to 1 in 2500	4
1 in 2500 to 1 in 3000	5
1 in 3000 to 1 in 3600	6
1 in 3600 to 1 in 4200	7
1 in 4200 to 1 in 4700	8
1 in 4700 to 1 in 5300	9
1 in 5300 to 1 in 6000	10
1 in 7000	12
1 in 8000	15
1 in 10,000	18

Note.—(1) The number of strokes required to give the standard colour at concentrations lower than those given in the table is roughly inversely proportional to the concentration present; an approximate estimate may be made by extrapolation from the above figures.

(2) The standard colour is that given by pure benzene. It may be found that crude benzoles give a slightly different shade of colour, but this should not interfere with the comparison of the depth of colour of the reagent and standard.

Directions are given for a procedure for sampling the atmosphere from a space that is not readily accessible, or where there is a possibility of highly toxic concentrations of benzene vapour being present.

Food Investigation Board

THE COLD STORAGE AND GAS-STORAGE OF EGGS*

THE purpose of this Leaflet is to describe briefly the principles and relative merits of the cold storage and gas-storage of eggs.

PRECAUTIONS IN SELECTING AND HANDLING EGGS FOR STORAGE.—Preferably only infertile eggs should be stored and they should be cooled and stored as soon as possible. On no account should eggs be washed. *Any* method of washing increases the number of rots, especially green rots. Stored eggs should be de-chilled artificially (in rapidly moving air at 50° F.) and consumed within a short period after removal from storage.

DETERIORATION DURING STORAGE.—The changes that may occur are:—(*a*) Growth of moulds on the shell; (*b*) penetration of shell by moulds and bacteria whose growth produces rots; (*c*) uptake of odours; (*d*) enlargement of air-cell and toughening of the shell membranes; (*e*) shrinkage and liquefaction of the thick white; (*f*) yellowing of the white; (*g*) weakening of yolk-membrane, (*h*) weakening of the yolk; (*i*) development of "storage taste." Some of these changes can be prevented, others only retarded. Control of atmospheric composition (including humidity) can prevent some and retard others.

COMPARISON OF METHODS OF STORAGE.—The following methods have been critically compared at the Low Temperature Research Station, Cambridge:—(i) Cold storage with control of humidity only; (ii) partial gas-storage (cold storage with control of humidity and addition of 2 to 2·5 per cent. of carbon dioxide); (iii) full gas-storage (cold storage with addition of 60 to 100 per cent. of carbon dioxide but no control of humidity).

The results refer only to selected, first-quality, unwashed eggs, held for 4 days at about 52° F. before storage. The characteristics of eggs stored by the three methods for periods between 6 and 9 months were as follows:

Cold storage	Partial gas-storage	Full gas-storage
Shell, smooth	Shell, slightly rough	Shell, slightly rough
Air-cell, large	Air-cell, large	Air-cell, small
White, distinctly yellow	White, faintly yellow	White, faintly yellow
Thin white, viscous	Thin white, viscous	Thin white, watery
Thick white,[1] weak (vol. 60–70 per cent. of new laid)	Thick white,[1] firm (vol. 60–70 per cent. of new laid)	Thick white,[1] firm but considerably shrunken[3] (vol. 40–50 per cent. of new laid)
Yolk, flabby	Yolk, firm	Yolk, firm
Storage taste[2]	No storage taste	No storage taste

[1] The amount of thick white depends not only on the method of storage but also upon the amount initially present; if it is large, the amount after storage will be correspondingly high.

[2] Shows up particularly in boiled eggs.

[3] Shows up particularly in water-poached or fried eggs, but not in steam-poached eggs.

Cold storage gives satisfactory results for periods up to about five months. Partial gas-storage has advantages over cold storage, notably prevention of development of "storage taste." In full gas-storage the white becomes very watery, but, on the other hand, this method is the most effective of the three in preventing rots; it cannot, however, prevent rots developing during marketing, since it does not always destroy the micro-organisms causing green whites, though it stops them growing during storage.

The Leaflet concludes with an outline of the main features of the three methods and a list of references to scientific literature.

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* Leaflet No. 8. By T. Moran, D.Sc., Ph.D. 1939. Department of Industrial and Scientific Research, 16, Old Queen Street, Westminster, S.W.1.

Queensland

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE, 1938

In his Annual Report Mr. F. Connah, F.I.C., states that 14,447 samples were examined as compared with 15,421 in the previous year. The Government Laboratory undertakes work for all the Departments of Public Service except the Department of Agriculture and Stock, which has its own laboratory and staff. The points of interest to which attention is directed include the following:

MILK CONTROL.—The methods now in use comprise the freezing-point determination, the methylene blue test, the use of the "Minit" apparatus to measure visible dirt, and, since 1935, the phosphatase test, to distinguish milk pasteurised at 142° F.—the minimum temperature prescribed under the Queensland Food and Drug Regulations.

The fine laid down in the Health Act for the watering of milk is £1 for each per cent. of added water.

COAL-TAR DYES IN BEVERAGES.—It cannot be accepted that any coal-tar dye in the quantity found in some beverages is entirely harmless to the human organism. The use of even the permitted dyes should be limited as far as possible. The minimum quantity required to enhance sufficiently the appearance of various cordials and beverages for trade purposes may be determined, and it is suggested that no more than that amount should be permitted. Fruit beverages of the same type contained coal-tar dye in quantities ranging from ½ to 4 grains per pint. If the former amount was sufficient, the latter must surely be regarded as excessive.

METALLIC CONTAMINATION OF SODA WATER.—Fifteen samples of soda water from soda fountains were examined, with the following results:—Lead was present in 9 samples in amounts ranging from 1/77th to 1/5th grain per gall., and in 4 in amounts from 1/1000th to 1/100th grain per gall. Copper (in addition to lead) was present in the 13 samples in amounts of 1/100th to 1/5th grain per gall. One sample, reported to have caused sickness and vomiting in children and adults, contained zinc in the proportion of 4 grains per gall.

APPARENT LOSS OF PHYTIN IN BREADMAKING.—In using the phytin-content as a factor in calculating the proportion of whole meal in bread, it was found that there was an apparent loss of phytin during baking. Controlled baking tests gave the following results:

	Whole meal			Whole meal + 25 per cent. of bran			
	Flour	Dough	Bread	Flour	Dough	Bread	Bran
Total phosphorus, per cent.	0·35	0·35	0·36	0·60	0·60	0·63	1·34
Phytin phosphorus, per cent.	0·33	0·30	0·26	0·62	0·54	0·42	1·50
Phytin, per cent. ..	1·17	1·07	0·92	2·2	1·92	1·50	5·3

As there was no loss in the total phosphorus, it would appear that, under the influence of fermentation and baking, some of the phytin is so changed that it no longer registers as phytin.

SWEET POTATOES.—The yellow variety of sweet potatoes is not generally popular, although it has a good flavour and has been found to contain up to 16,000 International Units of vitamin A per lb., whereas the popular white variety is deficient in vitamin A. The percentage composition of samples of sweet potatoes and "English" potatoes from the local market was as follows:

	Sweet potatoes		"English" potatoes (Carmen)	
	Yellow variety	White variety	Stanthorpe	Forest Hill
Water	68·0	77·0	78·6	77·0
Protein	1·3	1·3	1·8	1·7
Ethereal extract (fat)	0·3	0·2	0·2	0·2
Sucrose	2·8	1·2	0·3	0·3
Invert sugar	0·5	2·8	nil	0·4
Crude fibre	0·9	0·7	0·5	0·6
Starch	25·1	16·0	17·6	18·8
Ash	1·1	0·8	1·0	1·0
	100·0	100·0	100·0	100·0
Phytin	0·13	0·13	0·1	0·18
Calcium (Ca)	0·026	0·013	0·0043	0·01
Phosphorus (P)	0·04	0·04	0·04	0·057
"Digestible calories," per lb.	550	390	366	360

Further work is necessary before the higher water-content of the white variety can be accepted as usual for sweet potatoes.

Acetanilide in Headache Powder.—Acetanilide is a poison under the Queensland Poisons Regulations. Any package containing it must bear a label with the word "Poison" and "Unfit for children under 16 years." *The British Pharmaceutical Codex* states that some persons are extremely susceptible to acetanilide, and that even small doses will lead in these cases to cyanosis and collapse. It has been excluded from the British Pharmacopoeia.

Vitamins in Cosmetics.—In a world made vitamin conscious it was to be expected that vitamins would ultimately be incorporated in cosmetics. The use of vitamins A and D in cosmetic cream probably finds its origin in the beneficial effect of cod-liver oil on burns and other skin lesions. Samples of such creams said to contain 20,000 units of vitamin A per lb. were examined.

Soluble Lead in Paint.—Under the Health Act, 1937, it is not permissible to use any paint containing more than 5 per cent. of soluble lead upon verandah walls, gates, steps, etc., of any house or building, or upon any fence whatsoever, or upon any other exterior portion of any building to which children under the age of 14 years have easy access.

Paint containing any lead may not be used on the roof of any house or building.

Of the 102 samples of paint examined, 75 contained over 5 per cent. of soluble lead, 9 contained less than 5 per cent., and 18 were free from lead.

British Standards Institution

The following Standard Specifications have been issued:*

No. 823—1938. British Standard Density—Composition Tables for Aqueous Solutions of Sodium Chloride and of Calcium Chloride for use in conjunction with British Standard Density Hydrometers.

The hydrometers and tables together provide a simple means of determining the strength of any given aqueous solution of sodium chloride or of calcium chloride or of making up a solution of known strength.

The appendixes to the tables give details of the British Standard density hydrometers available for such solutions, a note on the reading of standard density hydrometers in the solutions, examples of the use of the tables, and details of corrections to readings. It is often adequately accurate to take the reading at any temperature $t°$ C. as giving directly the density of the solution in g. per ml. at $t°$ C.

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* Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net, post free 3s. 8d., each.

No. 824—1938. BRITISH STANDARD DENSITY-COMPOSITION TABLES FOR AQUEOUS SOLUTIONS OF CAUSTIC SODA FOR USE IN CONJUNCTION WITH BRITISH STANDARD DENSITY HYDROMETERS.

From the density determined at any particular temperature the tables enable the density and composition of the caustic soda solution to be determined at any temperature within the range of the tables.

Appendixes give details of the British Standard density hydrometers available for aqueous solutions of caustic soda, a note on the reading of the hydrometers in these solutions, examples of the use of the tables, and details of corrections to the readings.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Starch-Iodine Coloration as an Index of Differential Degradation by the Amylases. C. S. Haines and M. Cattle. (*Proc. Roy. Soc.*, [B], 1938, **125**, 387–414; *J. Inst. Brewing*, 1939, **45**, 70–71.)—Iodine coloration was followed with a view to correlating it with enzymic breakdown by different amylases—α malt, *Aspergillus*, salivary, pancreatic, and β amylase. Absorption spectra were determined at intervals during the action of the amylases on starch, and the liberation of reducing groups was followed by means of both alkaline copper and alkaline hypoiodite reagents. A soluble starch substrate, as prepared by Small (*J. Inst. Brewing*, 1919, 180), was used, and the method of preparing the amylases is described in an appendix. The concentration of starch was 0·2 per cent. and the temperature of conversion 25° C. The so-called saccharogenic and dextrinogenic types of amylase can be distinguished almost from the beginning of their action by the manner in which the absorption characteristics of the iodine compounds are altered, and during each degradation process the relation between the changes in the iodine-colouring property and the liberation of reducing groups can be delineated accurately. The observations can be explained by two hypotheses. According to the first, a single species of "colouring group" would be considered to occur at regular intervals along the chain structure, and the absorption characteristics of the compound formed by the attachment of iodine at this group would depend upon the mode or degree of association of the molecular chains of a particular product. According to the second hypothesis, two or more distinct species of "colouring group," yielding compounds of different hue, might be assumed to be distributed in parallel along the chains, but of these, one species at least would be assumed to exist exclusively in molecular associations. Both of these theories incorporate the conceptions that the "colouring groups" are distributed homogeneously along the molecular chain structure, so that different portions of the molecule are approximately equivalent in this respect, and that differences in the hue of iodine colours exhibited by different products are related mainly to the phenomenon of molecular association. On either theory, the alterations in iodine colour observed during the action of β-malt-amylase are conceived as resulting from a progressive reduction in the number of "colouring groups" during the cleavage of maltose fragments from the end of the chain. The fact that the intimate molecular associations of the residual dextrins are not broken down during this process would account for the approximately constant absorption characteristics of the iodine compounds. Conversely, with the dextrinogenic amylases, the marked alteration in the hue of the iodine colour is attributed mainly to a preliminary disruption of molecular associations, this being followed by a progressive destruction of "colouring groups" as the chains are cleaved into achroic dextrins. E. M. P.

"Iles Mannan Flour." J. E. De Groot, C. J. Van Hulssen and D. R. Koolhaas. (*Chem. Weekblad*, 1939, **36**, 69–73.)—The product known as "iles mannan flour" in the Dutch Indies is prepared from the tubers of varieties of the *Amorphophallus* family (*i.e. A. campanulatus, A. oncophyllus, A. variabilis, A. spectabilis, A. decus silvae* and *A. muelleri*). The tubers should be gathered in their second year of growth, when the leaves have withered and the tubers have attained their maximum diameter (about 20 cm.). They are dried, cut into slices and ground finely, and they then undergo a combined stamping and winnowing process which eliminates the cell walls and raphides (needle-shaped crystals of calcium oxalate). The raphides are particularly abundant in the wild plants; they are objectionable when (as in Japan) the flour is used as a foodstuff. *A. rivieri* ("devil's tongue") is processed in this way in Japan, and the resulting flour (which is known as "konjaku flour") has a mannan content (determined viscosimetrically, see below) of 60 per cent. (calculated on the dry substance). The mannan contents of the Javan varieties listed above are approximately 5, 24·4 to 52·4 (mean, 35), 6·7 to 21·6 (mean, 14), 30, 9, and 14 per cent., respectively. Existing knowledge of the chemistry of mannan is reviewed (*cf.* Haworth, *J. Chem. Soc.*, 1937, 784); Ohtsuki and Nishida (*Acta Phytochim, Japan*, 1928, **4**, 1) have shown that the mol. of konjaku mannan is built up from 1 mol. of glucose and 2 of mannose, whilst *X*-ray evidence (*cf.* Sakurada and Hutino, *Z. physik. Chem.*, 1933, **21**, 18) suggests that it can exist in two forms having different chemical properties. The flour is usually evaluated in terms of its mannan-content, but determinations, by means of phenylhydrazine, of the mannose produced by hydrolysis has not been found to give a reliable indication of the quality of the flour. The present authors prefer to determine the relative viscosity, as follows:—The tuber is slit, dried in a current of air at 40° to 45° C., ground finely, and passed through a 0·8-mm. sieve. The powder (1 to 2 g.) is then stirred with 300 g. of water at 55° C. for 2 hours, the water lost by evaporation is made good, and the solution is cooled to 27·5° C. and its relative viscosity determined at 27·5° C. A calibration curve relating the (Engler) viscosity and concentration of mannan was compiled from experiments with known quantities of mannan (see below) and is reproduced, and this may be used for actual determinations. Curves relating the viscosity and time of stirring are also reproduced; they show that the same maximum and constant viscosity is obtained under the above conditions as by stirring for 1 hour at 50° C. The temperature should not exceed 50° C., as otherwise the paste gels. The moisture-content of the flour should also be determined, *e.g.* by Aufhäuser's method of distillation with xylene (*Chem.-Ztg.*, 1922, **46**, 1149) because, if drying is carried too far, the colloidal structure of the flour is changed and low viscosities result. A rise in *p*H results in a fall in viscosity, and this also may be important when the flour is used as a creaming-agent in latex which may contain ammonia. Mannan contents (percentages as determined by a chemical method) and relative (Ostwald) viscosities, for 0·23 per cent. solutions of three such products respectively, are:—Mannan, 63·4 and 7·7; bittchu powder (a high grade of konjaku flour), 50·1 and 4·9; and ordinary konjaku flour, 54·7 and 2·7. Mannan may be purified (*cf.* Ohtsuki, *loc. cit.*) by stirring the flour with water at a temperature not exceeding 55° C., and adding alcohol to the viscous solution which is obtained on cooling. The resulting precipitate of gluco-mannan is separated, and redissolved and reprecipitated several times. It is finally suspended in a mixture of alcohol and ether and filtered. It is then obtained as a white or grey powder and free from reducing sugars. Hydrolysis with 5 per cent. hydrochloric acid produces reducing sugars, and the mannose may be determined by the phenylhydrazine method. The mannose-contents (percentages on the dry sample) and (Ostwald) viscosities of 0·23 per cent. solutions at 27·5° C. for the mannans obtained from 3 sources are, respectively:—From konjaku flour, 63·4, 7·7; from *A. oncophyllus*, 59·8, 7·8; from *A. variabilis*, 63·6, 3·3. Uses of iles flour are as a substitute for gelatin (in foodstuffs), for agar-agar (*e.g.* in culture media) and for starch (*e.g.* to confer water-resistance and impermeability on paper). It is also used in insecticides, in cosmetic preparations, as a creaming-agent for latex, and as a flocculating agent for coal slurrys; suspensions of clay are flocculated if sufficient quantities of a solution of the flour and of a sodium hydroxide solution are added to produce concentrations of 0·0025 per cent., and 0·002 *N*, respectively. J. G.

Colorimetric Method for the Determination of Sugars. E. A. Schmidt. (*Das Mühlenlabor.*, 1938, **8**, 122–131.)—This method was worked out for the purpose of estimating the small quantities of sugar (maltose) present in flours or formed in the course of bread-making. When maltose solution is heated with alkali caramelisation occurs, and when the experimental conditions are rigidly standardised the intensity of the brown colour is a measure of the sugar concentration of the solution. By comparison with standard solutions or by photometric methods the amount of the sugar present may thus be determined. The degree of caramelisation varies with the nature of the alkali used and follows the order potassium hydroxide, sodium hydroxide, sodium carbonate, ammonium hydroxide. A normal solution of sodium hydroxide was found to be most suitable for the determination. Experiments showed that within certain limits the concentration of alkali is of secondary importance but the effect of variations in sugar concentration is incomparably greater. The procedure is as follows:—To 15 ml. of the sugar solution, which should be diluted until the concentration of sugar lies between 0·06 and 0·8 per cent., 5 ml. of *N* sodium hydroxide solution are added and the mixture is heated in a boiling water-bath for exactly five minutes, in which time the brown colour reaches its maximum intensity. The colour is then compared with that produced by standard solutions of the pure sugar treated in the same way. For the determination of maltose the colorimeter of Schmidt and Kühn, in which the intensity of the brown colour is measured by means of standard coloured discs, is described. Under the standard conditions maltose, glucose, fructose, mannose, and arabinose are caramelised to the same extent. Lactose and galactose give somewhat deeper, and glycerose somewhat lighter colours. Sucrose, raffinose, starch, dextrin and the alcohols mannitol, sorbitol, etc., are not caramelised. Since the curve formed by plotting the degree of caramelisation against the concentration of sugar is not linear, it is necessary to employ a complete series of standard sugar solutions which are treated in the same manner as the sample solution to obtain the absolute amount of sugar present. When the solutions are matched in a colorimeter it is possible to obtain very exact results by the method. The albuminous constituents of flours, *viz.* amino acids, peptones and proteins do not interfere with the development of the colour and may be considered inert under the standard conditions of the method. A. O. J.

Cobalt-content of some Food Materials from different parts of the United States. Bashir Ahmad and E. V. Mc.Collum. (*Amer. J. Hyg.*, 1939, **29**, [A], 25–26.)—In view of the evidence that has accumulated in the last two years that traces of cobalt are essential for the nutrition of sheep and cattle and that cobalt deficiency may give rise to the so-called "coast disease," "bush sickness" or enzootic marasmus, the authors undertook a study of the cobalt distribution in some common foods collected from various parts of the country. They employed a modification of the colorimetric method of Stace and Elvehjem depending upon the formation of a stable red compound with nitroso-R-salt (nitroso derivative of 3·6-β-naphthol disulphonate). They found that considerable variation exists in the cobalt-content of different materials. On the whole leguminous seeds are richer than the cereal grains, the value for the former ranging from 0·018 to 0·0475 mg. and for the latter from 0·014 to 0·042 mg. per 100 g. of dry material. No correlation could be found between the cobalt-content and the sources of the food stuffs according to States; thus kidney beans from Colorado gave the highest value, whilst peas from the same State gave a somewhat low value. D. R. W.

Characteristics of Tobaccos of the Acid and Alkaline Groups. A. Wenusch. (*Z. Unters. Lebensm.*, 1939, **77**, 170–172.)—Tobacco smoke contains a number of substances which, during the burning, have been volatilised without change of chemical constitution, and these, together with other associated substances, influence the odour and taste of the smoke. Since these bodies, which belong to very diverse classes (*e.g.* higher hydrocarbons, resins, resin acids, nicotine, etc.), have different solubilities in different solvents, their partial separation can be effected by treatment of the finely powdered tobacco with these solvents. The tobacco is exhaustively extracted for several days in a Soxhlet apparatus with each of the following solvents:—Petroleum spirit, ether, alcohol, and water. After each extraction the solvent is removed by evaporation and the soluble residue is dried at 80° C. and weighed. After the final (aqueous) extraction the exhausted tobacco is washed with alcohol and ether, dried first at 80° C., and finally over phosphoric anhydride and weighed, and its volume is measured in a graduated cylinder. The bodies appearing unchanged in the smoke are extracted mainly by the non-aqueous solvents. Nicotine appears to be the only constituent of the aqueous extract occurring unchanged in the smoke. For the experiments five samples were used, *viz.* a very good and a somewhat inferior tobacco of each of the two groups and a dried but not fully ripened raw tobacco (Zihna) of the acid group. The petroleum spirit extracts of the tobaccos of the acid and alkaline groups showed little difference, but the ethereal and alcoholic extracts were lower for the alkaline group than for the acid group, whilst the aqueous extracts were higher for the alkaline group than for the acid group. The opinion previously expressed (*Z. Unters. Lebensm.*, 1938, **76**, 433), *viz.* that tobacco leaves intended for the preparation of commercial raw tobacco of the alkaline group must be collected at a less advanced stage of development than those of the acid group is now supported by the observation that commercial tobacco of the alkaline group yields more water-soluble extract than tobacco of the acid group in spite of differences in the process of manufacture, which tend to reduce water-soluble matter in the tobaccos of the alkaline group and to conserve it in those of the acid group. The volume of dried exhausted residue per 100 g. is much lower with tobaccos of the acid group than with those of the alkaline group. This also shows that tobacco leaves for preparation of the acid group are collected at a later stage of development. The percentage amounts of extract found with Nigritta, Class I and Nigritta Refuse (the figures for the latter being in brackets), both of the acid group, were:—(*a*) Petroleum spirit, 5·18 (6·77); (*b*) ether, 6·59 (5·37); (*c*) alcohol, 31·91 (24·52); (*d*) water, 16·22 (21·36); (*e*) insoluble residue, 39·96 (41·96); (*f*) volume of exhausted residue from 100 g., 116 (168) ml. For Havana of very good quality (and Havana of lower quality), both of the alkaline group, the corresponding figures were:—(*a*) 6·09 (5·08); (*b*) 1·67 (1·42); (*c*) 8·96 (11·30); (*d*) 33·15 (34·80); (*e*) 50·01 (46·89); (*f*) 286 (336) ml.; for the high-quality Zihna tobacco of the acid group the figures were:—(*a*) 6·60; (*b*) 5·63; (*c*) 35·31; (*d*) 19·05; (*e*) 32·63; (*f*) 108 ml.

A. O. J.

***p*H Value of Fermented Tobacco Leaves and Cigarettes. C. Pyriki.** (*Z. Unters. Lebensm.*, 1939, **77**, 157–170.)—Since the *p*H of tobacco varies only within narrow limits, its determination must be made with an accuracy of 0·01 to 0·02, and for this purpose the Ionometer of Lautenschläger (Kordatzki, *Taschenbuch der praktischen p*H-*Messung*, Munich, Verlag Müller und Steinicke, 1934, p. 68) is recommended for its simplicity and rapidity of application. Brückner (*Der Biochemie des Tabaks*, Berlin, Verlag Parey, 1936, p. 170) uses the combined calomel-quinhydrone electrode of Tödt with an extract prepared from 5 g. of powdered or shredded tobacco and 100 ml. of conductivity water under definite conditions, but the method takes much time. The method to be described is simpler and is applicable to a suspension of tobacco in distilled water. The powdered or shredded tobacco (0·5 g.) is thoroughly stirred with 10 ml. of distilled water for one minute and, after the addition of saturated quinhydrone solution, the stirring is repeated for ½ to 1 minute and the determination of *p*H value is made with observation of the temperature, the value being reduced to 18° C. by means of a curve. The results obtained agree well with those obtained by the method of Brückner. Although shredded tobacco may be used, powdered tobacco is preferable, the sample being dried at 30° C. for 3 hours before powdering. Experiments with a number of different tobaccos showed that those of *p*H 5·5 can be dried for 3 hours at 50° C. with little change of *p*H, and that those of lower *p*H are not affected by drying at 95° C., but a Java cigarette tobacco of *p*H 6·5 was affected to a greater extent even when dried at ordinary temperature over calcium chloride. It has already been shown (Pyriki and Dittmar, *Z. Unters. Lebensm.*, 1931, **61**, 216; Abst., ANALYST, 1931, **56**, 407) that oriental tobacco does not lose any basic constituents when dried at 50° C. It is known that the quality of fermented tobacco improves from the lower to the higher leaves of the plant, and since the hydrogen ion concentration of the cell sap increases with higher position of the leaf, it follows that the *p*H of good-quality tobacco is lower than that of poorer qualities. As a rule young fermented leaves have a higher *p*H than older leaves. Experiments with Macedonian tobacco leaves showed that as the leaf turns brown the *p*H falls. Attempts to correlate *p*H and size of leaf gave irregular results and probably could be successful only with leaves taken from the same plant. By a classification of leaves according to their probable position on the stem it was possible, in spite of certain irregularities, to say that towards the apex of the plant the acidity of the leaf increases. It has been shown (Pyriki and Dittmar, *loc. cit.*) that portions of the leaf near the tip are richer in nicotine and poorer in sugar than portions near the stalk, and Andreadis and Toole (*Z. Unters. Lebensm.*, 1934, **68**, 431; Abst., ANALYST, 1935, **60**, 110) found that the nicotine-content increases from stalk to tip and from midrib to margin. Experiments showed that the *p*H diminishes from tip to stalk and from margin to midrib independently of the position of the leaf on the stem. The results obtained show that according to age, ripeness and position of the leaf on the stem the range of variation of *p*H is 4·7 to 5·8, although in individual instances values of 4·5 and 6·0 were obtained. As a rule the *p*H of tobacco of high quality is lower than that of inferior grades, the high acidity producing mildness in the smoke by fixing the nicotine and other basic substances (Pyriki, *Z. Unters. Lebensm.*, 1932, **64**, 273; Abst., ANALYST, 1932, **57**, 727). Investigation of certain brands of cigarettes (478 samples of 27 brands) gave a *p*H range of 4·95 to 5·29. Cigarettes of higher quality had lower *p*H values than those of lower quality, and this was found to be true also of raw tobacco intended for the manufacture of cigarettes. As a rule, storage of cigarettes promotes an increase of acidity, and no essential difference was found with cigarettes packed in cartons and in metal containers. With lower-priced cigarettes the acidity increased more rapidly than with higher-priced brands. With cigarettes stored loose on a shelf a somewhat greater lowering of *p*H occurred. It appeared also that the higher the initial *p*H of the cigarette the more rapidly it diminished. The cigarettes stored in metal containers for 12 months were infected with moulds and had a musty odour; those stored in cartons had a musty odour but were free from mould. Both mould formation and mustiness were less evident in the higher-priced brands. A. O. J.

Biochemical

Determination of Creatinine and Creatine. 1. Determination in Urine. E. C. Noyons. (*Chem. Weekblad*, 1939, **36**, 63–68.)—Improvements in Jaffé's picric acid method (*cf.* Chapman, ANALYST, 1909, **34**, 475; Greenwald and Gross, *id.*, 1928, **53**, 400; 1929, **54**, 60) are discussed. The colour produced with this reagent may be evaluated satisfactorily in the Pulfrich step-photometer if the reagent and the creatinine to be used as a standard are prepared as follows:—To a boiling solution of 25 g. of anhydrous sodium carbonate in 600 ml. of water are added, in small quantities, 50 g. of technical picric acid. The mixture is boiled, filtered and cooled rapidly, and the resulting crystals are separated by filtration and washed well on the filter with 220 ml. of 12 per cent. sodium hydroxide solution. They are then shaken with 300 ml. of 10 per cent. hydrochloric acid, again filtered off, washed with water, dried at 100° C. and recrystallised at least twice from hot pure acetic acid. A solution in 10 per cent. sodium hydroxide solution should show no absorption in the step-photometer, using the S53 filter. The creatinine is purified by adding 15 ml. of a filtered, saturated solution of rufianic acid to a solution of 500 mg. of creatinine in a mixture of 10 ml. of water and 1 ml. of 5 per cent. sulphuric acid. After 3 days in the ice-chest the creatinine monorufianate is separated on a glass filter (G3) and recrystallised twice from water. The rufianic acid is then precipitated from a solution of the crystals in dilute ammonia by addition of finely-powdered baryta, followed by filtration, and removal of the excess of barium hydroxide by precipitation with a current of carbon dioxide and re-filtration. The pure creatinine is then obtained by evaporating the filtrate, a micro-determination of nitrogen being used to control its purity (*cf.* Zimmermann, *Z. physiol. Chem.*, 1930, **188**, 180; **189**, 155). A solution of 20 mg. of the pure creatinine in 100 ml. of water is then prepared, and 10-ml. portions (or 1 ml. diluted to 10 ml. where necessary) of this are taken. To 4 ml. of each solution are added 12 ml. of a saturated solution of picric acid, and to 10 ml. of this mixture are added 0·5 ml. of 10 per cent. sodium hydroxide solution (free from carbonate). The extinction of the solution is then evaluated in the step-photometer after 30 minutes, with the use of the S53 filter and at a depth of liquid of 30 mm. The relationship between the concentration of creatinine (0·2 to 3·2 mg. per 100 ml.) and the extinction is linear, and a graph (which is reproduced) is used for the evaluation of samples of unknown concentrations. Since the Jaffé reagent is not specific for creatinine, the following methods for the isolation of the creatinine are described, together with the experiments that justify their adoption:—(1) *Extraction.*—The sample is extracted with 10 ml. of warm *iso*butanol or *iso*pentanol, and to the extract are added 10 ml. of a mixture of 15 ml. of the picric acid reagent, 5 ml. of water, and 10 ml. of 10 per cent. sodium hydroxide solution; the resulting colour is matched as usual. Under certain conditions, however, extraction of the creatinine may not be complete, and the solvent may not be entirely selective for creatinine. (2) *Adsorption.*—A mixture of 1 ml. of the filtered urine and 9 ml. of water containing 0·5 g. of acid clay is shaken for 2 minutes and centrifuged, the liquid is poured off, and the operation is repeated, first with 3 ml. of water and then with 10 ml. of 1 per cent. sodium hydroxide solution. The last operation elutes the creatinine, and the liquid which separates should be neutralised with 25 per cent. hydrochloric acid and diluted to 100 ml. in a graduated flask. The colour is then allowed to develop in a mixture of 2·5 ml. of this solution with 7·5 ml. of the reagent and 0·5 ml. of the alkali; larger quantities of alkali than this give high results. To test the suitability of the acid clay 0·5 g. should first be shaken with 10 ml. of a solution of 20 mg. of creatinine in 100 ml. of 0·25 per cent. hydrochloric acid, the separated liquid being rejected and the clay washed twice by shaking and centrifuging with two 3- and one 1-ml. portion of water. The last wash is tested colorimetrically for creatinine, which should be absent, and the clay is then eluted as described above; if a determination shows that all the creatinine has been recovered, the clay is satisfactory. This method has been tested exhaustively, and full data regarding the adsorbing properties and selectivity of common adsorbing agents are provided; acid clay is shown to be the only one that fulfils the requirements of the method. Creatine and creatinine in urine are determined by evaporating 1 ml. on the water-bath with 0·1 ml. of 25 per cent. hydrochloric acid, and treating a solution of the residue in 10 ml. of water with acid clay, etc., as described above. This process converts the creatine into creatinine, so that the difference between the creatinine-contents before and after applying it gives the creatinine derived from creatine; the factor 1·16 then gives the latter. Comparison with the Lieb and Zacherl method (*id.*, 1934, **223**, 169; 1935, **232**, 41) for urines containing known quantities of creatine and creatinine showed that the latter method gives very high results, the errors with the new method being only +0·7 to −0·8 mg. for 5 to 15 mg. of creatinine. (3) *Precipitation.*—One ml. of 25 per cent. hydrochloric acid is diluted to 100 ml. with the urine in a dry measuring flask, and after filtration 10 ml. are mixed with 5 ml. of a 5 per cent. solution of phosphotungstic acid; after the mixture has stood for 3 hours, it is filtered. A portion (*e.g.* 1·5 ml.) of the filtrate, and also of a mixture of 10 ml. of the unprecipitated solution and 5 ml. of water, is diluted to 100 ml., and 2·5 ml. of each of these new solutions are mixed with 7·5 ml. of a saturated solution of picric acid and 0·5 ml. of 10 per cent. sodium hydroxide solution. The colours are matched in the usual way, and the difference between the two values found from the curves gives the true creatinine-content. For the determination of creatine, 10 ml. of urine are evaporated with 1 ml. of the acid, a solution of the residue in exactly 10 ml. of 1 per cent. hydrochloric acid being treated as described above; the resulting creatinine value includes that derived from the creatine. The use of 3·5-dinitrobenzoic acid (*cf.* Langley and Evans, *J. Biol. Chem.*, 1936, **115**, 333) was also examined, but was found too dependent on working conditions to provide a reliable and yet rapid method. J. G.

Occurrence of Zinc in Human Blood. F. H. Vogelenzang. (*Pharm. Weekblad*, 1939, **76**, 89–99.)—The importance of zinc in the vegetable kingdom and its function in the human organism are discussed (*cf.* Zbinden, *Compt. rend.*, 1929, **188**, 1628) and analytical methods applicable to such investigations are outlined. There is a full bibliography. In the method of determination now recommended (*cf.* Hibbard, *Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **10**, 127) the sample (*e.g.* blood) is evaporated on the water-bath, dried at 120° C., and ignited at 490° C.; so long as the temperature of ignition is below 500° C. there is no risk of losses by volatilisation. The dithizone reagent used (*cf.* H. Fischer, ANALYST, 1937, **62**, 150) is prepared by shaking a solution of 15 mg. in 100 ml. of carbon tetrachloride with 0·02 *N* ammonia, the aqueous layer being subsequently acidified, and re-extracted with sufficient carbon tetrachloride to bring the concentration of dithizone to 6 mg. per 100 ml.; dilution of the strong stock solution in this way should be carried out every day. To a solution of the ash in 5 ml. of 2 *N* hydrochloric acid are added 2 ml. of a solution of citric acid, from which any lead, copper or zinc has been removed by making a 10 per cent. solution weakly alkaline to litmus with 25 per cent. ammonia and extracting with successive portions of the dilute dithizone reagent until the carbon tetrachloride layer is coloured green. Pyrex glass vessels are recommended for all these operations, as some glasses (*e.g.* normal Jena glass) contain zinc. The solution is then made weakly alkaline to litmus with 2 *N* ammonia and extracted with small separate portions of the dilute dithizone reagent, until the carbon tetrachloride layer is green. The combined extracts are then shaken with two 5-ml. portions of 2 *N* hydrochloric acid, which causes the zinc to pass into the acid layer, leaving the copper in the carbon tetrachloride; the effects of lead in blood may be ignored, as the amounts concerned are normally too small to affect the results. The acid solution is made weakly alkaline with 2 *N* ammonia and again shaken with the dilute dithizone reagent, and the carbon tetrachloride layer then contains the red zinc-dithizone complex, with an excess of reagent which may be removed by shaking with 0·02 *N* ammonia. The carbon tetrachloride layer is then washed with water and filtered through a dry paper, any residue being washed with the solvent. The united filtrate and washings are diluted to a known volume with the solvent, and the colour is matched in a Pulfrich photometer against a standard prepared in a similar way from pure zinc sulphate. It was found that the coloured solution obeys the Lambert–Beer law, and that its absorption spectrum indicates a maximum absorption at $525 m\mu$; the colour filters S53 (green) and S47 (blue) may therefore be used, and the necessary extinction-coefficients are given. Direct extraction of the sample after treatment with trichloroacetic acid and filtration gives results similar to those obtained by ignition. It is necessary, however, to allow for a blank determination on the reagent, and trouble from the formation of an emulsion may also result. The amounts of zinc in the venous bloods from 30 patients are recorded, the values obtained being 0·34 to 0·90 (average, 0·612) mg. per 100 ml. for patients having diabetes mellitus, and 0·23 to 1·03 (average, 0·604) mg. per 100 ml. for others. The highest value recorded was obtained in a case of polycythemia, and the lowest in a severe case of hyperchromic anaemia. Tests on 10 samples showed that as a rule 88·6 to 92·2 per cent. of the zinc is contained in the blood cells, the remainder being in the plasma, but with 3 diabetics 100, 93·2 and 95·4 per cent., respectively, was found in the blood cells. In 2 cases of myeloid and lymphatic leucaemia, the amounts of zinc in the white cells were 0·193 and 0·091 and in the red cells, 0·39 and 0·43 mg. per 100 ml., respectively. The distribution of the zinc-contents of 27 samples showed averages of 0·52, 0·605 and 0·70 mg. per 100 ml., for those with less than $4{\cdot}3 \times 10^6$, $4{\cdot}3 \times 10^6$ to $4{\cdot}8 \times 10^6$, and more than $4{\cdot}8 \times 10^6$ erythrocytes, respectively, and it is concluded that the amount of zinc in blood is probably related to the number of cells present. J. G.

Influence of Zinc on the Reaction between Iodine and Insulin. E. H. Vogelenzang. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 201–206.)—The iodine-consuming power of insulin was measured at *p*H 7·2 in the presence of calcium, cadmium, aluminium, zinc and lead; cobalt, nickel, copper and iron were excluded to avoid complications of the reaction. Two methods were used: (1) To a solution of the proteins was added a solution of the cation, and the pH was brought to 7·2 with a sodium phosphate buffer. An excess of iodine was added, and the unused iodine was titrated after a convenient time. (2) An insufficient quantity of iodine containing starch was added to the buffered solution, and the time required for decolorisation was measured. Ovalbumin (dried egg albumin), human serum, pancreatin (U.S.P.), pepsin (Witte), peptone (free from fibrin), and four insulin preparations (A, amorphous insulin—1 unit in 0·079 mg., about 75γ of zinc per mg.; B, crude insulin—1 unit in about 0·75 mg.; C, crude insulin—1 unit in about 1·7 mg.; D, crystalline insulin—1 unit in 0·042 mg., about 35γ of zinc per mg.) were used. Solutions were prepared containing 0·1 per cent. of dry substance in 0·005 N hydrochloric acid. Calcium chloride, cadmium chloride, zinc sulphate, zinc acetate and lead acetate were used in 0·004 molar concentrations, and aluminium sulphate in 0·0027 molar concentration. These solutions were calculated to contain the equivalent of 65γ of zinc in 0·25 ml. This quantity is sufficient to account for about 45 units of insulin. The buffer solutions used were 0·2 molar disodium hydrogen phosphate and disodium hydrogen phosphate-sodium dihydrogen phosphate mixtures of the same concentration. The iodine solutions were prepared by diluting 0·1N solution with water. The mixtures were acidified with phosphoric acid and titrated at 15° to 20° C. with 0·005 N sodium thiosulphate solution; the uncertainty of the titrations did not exceed 0·04 ml. The influence of pH was found to be negligible for small variations from 7·2.

Influence of zinc on the iodine-consuming power.—To 2·5 ml. of solution were added 0·25 ml. of zinc solution and 0·35 ml. of phosphate solution; in a second series the zinc solution was replaced by 0·25 ml. of water. To the mixtures was added 0·5 to 1·0 ml. of 0·01 N iodine solution. After 15 minutes the solutions were acidified and titrated, starch being used as internal indicator. The following results show that the difference found for insulin must be ascribed to the influence of the added zinc.

Substance	Iodine, ml. 0·01 N			Difference
	Added	Combined after 15 mins.		
		Zn present	Zn absent	
Ovalbumin ..	0·50	0·36	0·35	0·01
Serum proteins ..	1·00	0·53	0·53	0
Pepsin	0·50	0·10	0·08	0·02
Peptone	0·50	0·35	0·35	0
Pancreatin	0·50	0·12	0·13	—0·01
Insulin A	1·00	0·51	0·59	—0·08

In further experiments it was found that the velocity of the reaction is influenced by the time at which the starch is added and by the ratio between starch and iodine. To obtain reproducible and constant results it is necessary to ensure a constant iodine-starch ratio by adding starch to the iodine solution. The addition of starch evidently lowers by adsorption the available iodine concentration. The quantity of iodine combined increases with time, and from 0·25 minute upwards (to 125 minutes) is a linear function of log. time. As the difference caused by the addition of zinc remains constant over a rather long period, the presence of zinc must be regarded as causing an inhibition of the action of iodine on a definite part of the insulin molecule and not as a retardation of the iodine-binding power of the insulin molecule as a whole, for in that event the difference would be expected to diminish gradually. The quantity of iodine combined, and the zinc effect, increase with physiological activity. The data presented are mainly of a qualitative nature. It was observed that a preparation of crystalline (zinc) insulin did not show the zinc effect after addition of extra zinc. The following facts suggest the possibility of a chemical method for the assay of insulin:—(1) The iodine-binding power of zinc-free and of zinc-containing insulin at *p*H 7·2 is probably a linear function of the physiological activity, and (2) the magnitude of the zinc effect is a function of the physiological activity of the insulin preparation. The latter method appears to be specific but is applicable only to zinc-free insulin, whereas the former may be of special value in the control of the industrial purification of insulin. With regard to the question as to which part of the insulin molecule is shielded by zinc, several considerations lead to the assumption that the zinc is bound to the sulphur of the insulin. E. M. P.

Bacteriological

Observations on Bacterial Growth in presence of Silver Foil. C. Siebenmann. (*Amer. J. Hyg.*, 1939, **29**, [B], 36–44.)—In contrast with the bactericidal action exerted by large silver surfaces in water, silver foil when added to broth is shown experimentally to have no growth-inhibiting influence on 15 out of 16 pathogenic micro-organisms tested. Only on one organism, the gonococcus, which is particularly sensitive to silver ions, was a small growth-retarding effect observed. These results are in accordance with the fact that sterilisation of water by silver surfaces is unsatisfactory if the water contains much organic matter. The author found that in Long's synthetic medium the growth of *B. coli* was inhibited by silver foil. In the experiments recorded the author has found that the silver foil is a good indicator for the formation of hydrogen sulphide, sulphides and polysulphides, the silver foil becoming discoloured whilst the controls remain bright. The results of the silver-foil test in broth cultures of 18 pathogenic organisms are recorded. The liberation of sulphides apparently depends partly upon the medium used. Thus while they were liberated with Difco Proteose Peptone by the coryne bacteria, they were not liberated with Parke Davis's peptone; with the latter, *B. suipestifer*, *B. typhosum*, *B. paratyphosum* A and *B. schottmülleri* (B) showed sulphide formation, and *S. haemolyticus*, *C. diphtheriae*, *C. xerosis*, *C. hoffmann staphylococcus aureus* and *pneumococci* showed none. D. R. W.

Longevity of Yeast. L. Fletcher and T. Mason. (*J. Inst. Brewing*, 1939, **34**, 96.)—Reference in the literature to cases of longevity of yeasts are not very frequent, but Chaston Chapman records the recovery of living yeast-cells from old beer deposits after 51 years and Hopkins and Hunter record recovery from bottled beer 49 years old. The classical method of preservation of pure cultures is in 10 per cent. sucrose solution, but in 1922 Ling recorded the recovery of living yeast from pure cultures kept on cotton-wool in Freudenreich flasks, eight in all, which were sealed up by Hansen in 1887—34 years previously. The authors have recently recovered living yeast-cells from a pure culture of

S. cerevisiae, Burton type, prepared by Ford in 1894, and after a little time-lag obtained vigorous growth. The properties of this culture at the time of isolation were carefully described by Ford and included the times taken for the appearance of ascospores under standard conditions at different temperatures. The authors have repeated the work on the revived 44-years-old culture and have found that the times of sporulation agree very well with those previously given. Moreover another pure culture of Burton yeast, which was originally isolated in 1894 and has been subcultured regularly up to the present time, has been examined by the authors and found to be very similar in appearance and in sporulation to the parent and sister cultures. It is of more than passing interest that an organism such as yeast should be capable of retaining its vitality and characteristics over a period of 44 years. D. R. W.

Microscopical Differentiation of Yeast Cells and Starch Grains by Differential Staining. E. Schmidt. (*Das Mühlenlabor.*, 1938, 8, 140–142.)—In the examination of cattle fodder and poultry foods it is frequently necessary to decide whether the product contains starchy material derived from bread, pastry and similar substances. Since these products almost invariably contain starch from other sources and since the starch derived from baked products is frequently gelatinised, the detection of yeast cells is almost impossible unless they are made prominent by staining. Although treatment of the preparation with iodine in potassium iodide solution colours the starch grains blue, the faint yellow colour imparted to the yeast cells does not give them sufficient prominence. If, however, the preparation is counterstained with carbolfuchsin the yeast cells are stained red and are easily found among the violet-blue starch grains. The procedure is as follows:—A small crumb of the material is moistened with water on the microscope slide and rubbed vigorously in order to disengage the starch grains and yeast cells from the gluten and other coarse materials, which may be gathered together and removed from the liquid. If the presence of fresh yeast is suspected the preparation is warmed slightly to kill the cells, which then absorb the stain more readily. Undue gelatinisation of the starch grains may be prevented by the addition of a little alcohol. If time permits, the preparation is allowed to dry. Iodine in potassium iodide solution is added until the starch is uniformly stained, excess being avoided since iodine decolorises fuchsin. A few drops of carbolfuchsin are added and the preparation is thoroughly stirred. If the liquid portion of the preparation is stained too deeply the yeast cells are less prominent and the colour should be reduced by the cautious addition of dilute iodine solution. With skill and practice the staining can be so regulated that the cherry-red yeast cells stand out clearly in contrast with the violet-blue starch grains. A. O. J.

Agricultural

New Constituents of Derris Root. I. Th. M. Meyer and D. R. Koolhaas. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 207–217.)—The isolation and properties of a substance first discovered by Buckley (*J. Soc. Chem. Ind.*, 1936, **55**, 285T), and of a new optically active substance, termed derride, isomeric with Buckley's compound, and also of a second new substance and of *l*-toxicarol and sumatrol from samples of derris root are described. The so-called derris resin, the ethereal extract of derris root of the type of *Derris elliptica*, freed from rotenone as far as possible by the ordinary method of analysis, was dissolved in ether and extracted 6 times with 0·5 per cent. sodium hydroxide solution. The ethereal layer was washed with water, shaken with dilute hydrochloric acid, washed twice with water, and evaporated, the last traces being removed *in vacuo*. The residue was dissolved in ethyl acetate, petroleum spirit was added, and carbon dioxide was passed through the solution, which was stored, tightly stoppered, in the refrigerator. After a week there was collected a material which after repeated recrystallisation from alcohol and ethyl acetate melted at 183° to 185° C. (at 183° C. it sintered) and had $[\alpha]_D - 2{\cdot}7°$ (in benzene). A mixed melting-point determination with a sample of Buckley's substance gave no depression. The authors and also Harper (*J. Soc. Chem. Ind.*, 1938, **57**, 1059) suggest that this compound has the structure of *iso*rotenone, from which the *iso*propyl group is absent.

Isolation of Derride from Derris Root.—A weight of 1·620 kg. of derris root was exhaustively extracted with ether and there was collected 24·8 g. of a solid material which separated during the extraction. After concentration of the extract there was obtained a very sticky residue which after treatment with methyl alcohol and ethyl acetate gave 25·6 g. of a white solid, which was recrystallised from methyl alcohol, giving a substance crystallising in needles and having m.p. 162° to 163° C., and $[\alpha]_D - 19°$ in benzene, $+13{\cdot}7°$ in acetone. Analysis of the material dried at 100° C. in a high vacuum gave: C, 68·60, 68·61; H, 4·74, 4·61; methoxyl (determined according to Vieböck and Brecher, *Ber.*, 1930, **63**, 3207), 17·94, 17·84 per cent.; $C_{20}H_{16}O_6$ requires C, 68·18, H, 4·56, methoxyl, 17·61 per cent. The new compound is readily soluble in benzene, ethyl acetate and carbon tetrachloride, and sparingly soluble in methyl alcohol or ether.

Isolation of l-*Toxicarol and Sumatrol from Derris Root.*—The powdered root (750 g.) was extracted with ether, and a solid (about 16 g.) which separated during the extraction, and on keeping the concentrated ethereal extract in a refrigerator for a few days, was collected. When recrystallised from cyclohexane and acetone it gave a yellow-green precipitate which was recrystallised from methyl alcohol. On treatment with benzene part of the substance dissolved; the residue was recrystallised from methyl alcohol and then from benzene, and gave crystals melting at 244° C. and with $[\alpha]_D + 107°$. Analysis of the material dried at 100° C. in a high vacuum gave: C, 65·33, 65·24; H, 4·50, 4·49 per cent.; $C_{20}H_{16}O_7$ requires C, 65·22; H, 4·43 per cent. From the mother liquor of this substance sumatrol was separated and purified by repeated recrystallisation from methyl alcohol; for the final purification use was made of the fact that sumatrol is moderately soluble in benzene, whilst the yellow material with which it is contaminated is very sparingly soluble. It had m.p. 195° to 196° C. and $[\alpha]_D - 184°$ in benzene. Analysis gave: C, 67·30, 67·49; H, 5·49, 5·58 per cent.; $C_{23}H_{22}O_7$ requires C, 67·31; H, 5·37 per cent. On treating with methyl alcohol and ethyl acetate the very viscous concentrated ethereal extract from which the first solid had been removed, about 30 g. of a yellowish-green substance separated on standing in the refrigerator. This was washed with a small quantity of methyl alcohol and ethyl acetate and recrystallised from ether; it had m.p. 98° C. and $[\alpha]_D - 70°$. With ferric chloride it gave a dark green colour. It was probably *l*-toxicarol (Martin and Tattersfield, *J. Soc. Chem. Ind.*, 1936, **56**, 77). From the mother liquor from this substance there was deposited impure sumatrol which, after recrystallisation from methyl alcohol, had m.p. 183° C. and $[\alpha]_D$−176·5°, and gave a deep brown colour with ferric chloride.

E. M. P.

Organic

Sodium Saccharin as a Reagent for Identification of Alkyl Halides. L. L. Merritt, Jr., S. Levey and H. B. Cutter. (*J. Amer. Chem. Soc.*, 1939, **61**, 15–16.)—Sodium saccharin reacts with alkyl halides to give *N*-alkyl saccharins, and when the reaction is carried out in butyl carbitol water well-crystallised derivatives are formed. No reaction occurs with tertiary compounds or branched chain chlorides. A mixture of 6 g. of sodium saccharin, 1 ml. of the alkyl halide, 25 ml. of butyl carbitol and 4 ml. of water are heated under reflux for 30 minutes, with the addition, with chlorides or methyl bromide, of 3·5 g. of potassium iodide. The mixture is then poured into 300 ml. of water and the suspension is cooled in an ice-bath. The *N*-alkyl saccharin usually crystallises, but if an oil forms it is separated, warmed until no odour of alkyl halide can be detected, and dissolved in hot alcohol, and water is added until a slight cloudiness results. On cooling, crystals are formed. The derivatives are recrystallised from aqueous alcohol. The yield varies from 0·5 to 0·8 g. except with *iso*butyl, when only about 0·25 g. is obtained and crystallisation is difficult. *n*-Propyl and *iso*butyl saccharin, and also allyl saccharin and bromoethyl saccharin have m.p. differing only by 1° C., but a mixture of the two shows in each instance a depression of 8° to 10° C. Ethylene dibromide requires to be heated under reflux for an hour. No derivatives could be obtained with methyl, ethyl, *iso*propyl, or secondary butyl chlorides, or with ethylene dichloride. The m.p. and elementary composition of a number of alkyl-group saccharins are given.

	Melting-points		
Alkyl group	Iodide °C.	Bromide °C.	Chloride °C.
CH_3	132	132	—
CH_3CH_2	94	94	—
n-C_3H_7	74	74	74
$iso C_3H_7$	134	134	—
n-C_4H_9	38–39·5	38	38
$iso C_4H_9$	75	75	—
s-C_4H_9	81	81	—
n-C_5H_{11}	58	58	58
$CH_2{=}CHCH_2$	—	98	98
$BrCH_2CH_2$	—	99	—
$C_6H_5CH_2$	—	—	110–111
p-$O_2NC_6H_4CH_2$	—	175·5	—

D. G. H.

Determination of Fumaric and Maleic Acids. S. C. Ganguly. (*J. Indian Chem. Soc.*, 1938, **15**, 611–614.)—By adapting the methods used by Szegedy (*Z. anal. Chem.*, 1937, **109**, 316), Frieman, Kennedy and Lucas (*J. Amer.*

Chem. Soc., 1937, **59**, 722), and Lucas and Pressman (*Ind. Eng. Chem., Anal. Ed.*, 1935, **10**, 149) fumaric and maleic acids may be determined in acid solution in the presence of succinic acid and phosphates, mercuric sulphate being used as catalyst. A flask containing a known excess of bromide-bromate mixture (10 to 15 per cent.) is evacuated, and 5 ml. of 6 *N* sulphuric acid are introduced and left for 2–3 minutes while the bromine is liberated, after which the flask is wrapped in a black cloth and the required quantities of 0·2 *N* mercuric sulphate and the solution to be analysed are run in, the wash-liquid not being allowed to exceed 10 per cent. of the total volume. The flask is well shaken and left in the dark for 30 to 35 minutes, after which 15 ml. of 2 *N* sodium chloride solution are added to liberate the bromine, followed by 5 to 10 ml. of 20 per cent. potassium iodide solution. The flask is then shaken for ½ minute, the vacuum is broken, and the liberated iodine is titrated with 0·02 *N* sodium thiosulphate solution. In comparing the mercuric sulphate method with Szegedy's method, it was observed that whereas high values were obtained with the latter in the direct halogenometric titration at a *p*H 8·4, low values were obtained when fumaric acid was titrated alone in acid solution in presence of phosphates, probably owing to HPO_4'' and H_2PO_4' being capable of catalysing the bromination of fumaric acid, whilst undissociated H_3PO_4 retards it.

D. G. H.

Glycerides of Japan Wax. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1939, **42**, 22–23B; *cf.* also *Bull. Chem. Soc. Japan*, 1931, **6**, 325, 337; 1935, **10**, 213; Abst., ANALYST, 1932, **57**, 266; 1935, **60**, 632.)—Dibasic acids (japonic acid) have already been shown to be present in Japan wax to the extent of 5·2 to 6·3 or even 7·1 per cent. of the mixed acids, and their main component to have the formula $C_{23}H_{44}O_4$. With a view to the isolation of these acids, glycerides with a concentration of the dibasic acids nearly four times that of the original wax have now been obtained. A petroleum spirit solution of the wax was chromatographically filtered through Japanese acid clay, with the result that the dibasic acid glycerides were more readily adsorbed than other glycerides, and thus accumulated in the upper layer of the clay. A further treatment of the clay after separation into the adsorbed and filtrate fractions was made and repeated four times, but the increase in dibasic acids was not marked after the second treatment, and the proportion of dibasic acids could not be made to exceed 24 per cent. It is suggested that the dibasic acids occur in Japan wax probably as mixed glycerides and in association with oleic acid. D. G. H.

Brassicasterol. Empirical Formula and Hydrogenation. E. Fernholz and H. E. Stavely. (*J. Amer. Chem. Soc.*, 1937, **61**, 142–143.)—Brassicasterol, a phytosterol isolated from an unrefined rape-seed oil of Japanese origin, has been found to be very similar to, but not identical with, stigmasterol. Analyses based on combustion of the bromides, on which the formula $C_{28}H_{46}O$ has previously been assigned, were not sufficiently accurate to distinguish between homologues, but the results obtained with the dinitrobenzoates were more reliable, even though the differences between the homologues were smaller. These results indicated that brassicasterol has the same empirical formula as stigmasterol, $C_{29}H_{48}O$, and not $C_{28}H_{46}O$ as given in the literature. Catalytic hydrogenation of brassicasterol yielded a saturated sterol not identical with that given by stigmasterol, so that the difference between these two compounds appears to lie in the carbon skeleton and not in the position of a double bond. D. G. H.

Pine-needle Extract and its Use. Anon. (*Chem.-Ztg.*, 1939, **63**, 99–100.) —Pine-needle extract contains the water-insoluble oil and the water-soluble extractives, including tannins, proteins, carbohydrates, resins, salts, bitter principles, plant acids and aromatic substances (*e.g.* aldehydes and ketones), as well as other substances of unknown nature present in pine-needles. It is prepared by digesting the ground twigs with hot water, removing the oil by steam-distillation, and evaporating the extract in a vacuum to a syrupy consistence. The oil is then stirred into the extract, the constituents of which serve to emulsify it. The conifers used are red fir (*Picea excelsa*), white fir (*Abies pectinata*), Scotch pine (*Pinus sylvestris*) and knee pine (*Pinus pumilio*). The corresponding oils differ in composition and in the character and intensity of their aroma, but the extractives are all similar, and their characteristics depend rather on the place of origin of the tree. The oil or extract is also marketed in the form of effervescing tablets, the other constituents of which are a bicarbonate and tartaric acid; or as a "milk," which is a colloidal solution or an emulsion of the oil (20 to 40 per cent.) in water, and which enables high concentrations of oil to be attained. These preparations, which have a soporific and sedative effect, are used principally in baths, and are beneficial for convalescents and in cases of rheumatism. Such baths should be taken at 34° to 38° C., and they should last 20 to 30 minutes and be followed by a rest-period of 90 minutes. It is believed that they increase the permeability of the skin towards inorganic salts and the oil; thus magnesium chloride added to the bath water could be detected subsequently in the urine of the subject. Good pine-needle extracts should contain 15 to 20 per cent. of tannin (see below), and they were used during the war as substitutes or diluents of tanning agents such as pine-bark or oak-bark extracts. The economics of this substitution are discussed (*cf.* Hübscher, *Pharm. Zentr.*, 1938, 665). The extract is marketed as a thick liquid (sp.gr. 1·25 to 1·3) which, when spread out on a glass plate and dried, should form a smooth, glazed, dark red-brown layer without cracking. The dry solids should not be less than 55 per cent., and the mineral substances approximately 5 per cent. The oil-content, as determined by steam-distillation, should be at least 1·5 per cent., and the ester-content of the oil, 5 to 25 per cent. (as bornyl acetate); the bornyl acetate content of the German oils is 4 to 10 per cent. although that of Siberian oils may rise to 40 per cent. When the equivalent of 10 g. of dry solids is diluted to 100 g. with water, it should give a strong foam on shaking, and a turbidity and a grey-brown precipitate should form. If a strip of filter-paper, 2 cm. wide, is immersed to a depth of 0·5 cm. in 5 ml. of the above-mentioned dilute solution, the maximum capillary rise of the liquid should be 4 to 8 cm., and the strip should appear light brown and have dark brown zones. Sulphite waste liquor, which is used as a diluent and adulterant, rises to above 8 cm. The water-insoluble matter of a genuine extract amounts to 2 to 3 per cent., and if the dry solids are determined on a 2 per cent. solution of the extract before and after filtration through a layer of weakly-chromed hide powder, the difference between the results gives the tannin-content (see above). Sulphur dioxide (from sulphite waste liquor) is detected by suspending a potassium iodate and starch paper in a loosely-stoppered flask containing 10 g. of sample and 20 ml. of water, and heating in a water-bath. If the blue colour is developed after addition of phosphoric acid, sulphur dioxide in combination is indicated. The blue colour is fugitive, but a positive reaction may be taken as indicating the presence of sulphite liquor, because sulphur dioxide is seldom used as a preservative for pine-needle extracts. If 5 ml. of a filtered 2 per cent. solution of the extract is treated with 0·5 ml. and then 2 ml. of conc. hydrochloric acid, the solution remains clear for at least 10 to 15 minutes if less than 5 per cent. of sulphite liquor is present; in the presence of more than 10 per cent. a turbidity and precipitate are formed (Hirst–Procter reaction). In filtered ultra-violet light the pure extract and sulphite liquor fluoresce with a dark olive-green and grey colour, respectively, mixtures giving intermediate shades.

J. G.

Inorganic

Gravimetric Determination of Copper. P. Spacu. (*Z. anal. Chem.*, 1939, **115**, 423–425.)—The method enables a quantitative separation of copper from manganese to be made. The neutral or feebly acid solution (strongly acid solutions should be nearly neutralised with ammonia), measuring 100 to 150 ml., is treated with 0·5 g. of ammonium nitrate and an excess of pyridine, heated to 30° to 40° C., and treated with excess of a cold conc. solution of ammonium or potassium dichromate. On cooling, the liquid deposits dark green crystals of the composition $[Cu(C_5H_5N)_4]Cr_2O_7$. The precipitate is collected in a porous porcelain crucible with the aid of a solution containing 0·3 g. of ammonium dichromate and 0·3 ml. of pyridine in 100 ml., and washed three times with the same mixture, then 2 to 3 times with 1-ml. portions of acetone containing 1 ml. of pyridine per 100 ml., and finally a few times with 2-ml. portions of ether. It is dried *in vacuo* over sodium hydroxide and weighed. Copper factor: 0·10673. W. R. S.

Volumetric Determination of Traces of Arsenic. J. Bodnár, E. Szép and W. Cieleszky. (*Z. anal. Chem.*, 1939, **115**, 412–420.)—The iodimetric microtitration of Gangl and Sánchez (ANALYST, 1934, **59**, 716) gives a negative error of less than 5 per cent. with quantities of 5 to 100γ. The authors recommend reduction with tin and hydrochloric acid (12 per cent. by weight) instead of zinc and sulphuric acid, the procedure requiring only 30 minutes instead of 2 hours with Gangl and Sánchez's evolution apparatus. The tin sponge is prepared from chemically pure stannous chloride dissolved in hydrochloric acid (1 : 1) and purest rod zinc placed in the solution. The sponge is washed with distilled water, and dried. The use of tin instead of zinc has the great advantage that antimony is not volatilised (ANALYST, 1935, **60**, 496); hence arsenic can be determined in presence of relatively large amounts of antimony by the modified procedure, the error not exceeding 5 per cent. W. R. S.

New Method of Separating Tin and Antimony and its Application to the Analysis of White Metals. U. Pelagatti. (*Chim. e Ind.*, 1938, **20**, 724–726.) —The method is based on the fact that in a medium acidified with dilute sulphuric acid and containing tartaric acid, the ferrocyanide of quadrivalent tin is insoluble whilst the ferrocyanide of tervalent antimony is soluble. The tin ferrocyanide is easily filtered off and contains no trace of the soluble antimony salt. The following procedure is recommended:—A quantity of the sample containing not more than 0·20 to 0·25 g. of tin and copper together (that is, 1 g. of white metals containing lead, or 0·3 to 0·4 g. of white metals with a tin base) is treated with 5 to 10 ml. of conc. sulphuric acid (according to the quantity of alloy taken) in a tall 200-ml. beaker of resistance glass covered with a watch-glass and heated on a sand-bath. After 10 to 15 minutes the liquid is cooled and diluted with 50 ml. of water containing 5 g. of tartaric acid. If lead is present, the liquid is allowed to stand until the lead sulphate has separated completely. The precipitate is collected in a weighed Gooch crucible, washed several times with a 5 per cent. solution of tartaric acid containing a few drops of conc. sulphuric acid and finally with alcohol, calcined in a double crucible, and weighed. The filtrate, or, in the absence of lead, the original liquid diluted finally to 100 ml. with water, is warmed to 60° C. and treated with an excess of potassium ferrocyanide (10 to 15 ml. of 10 per cent. solution), which precipitates the tin and copper as the ferrocyanides. If the temperature is higher than 60° C., the potassium ferrocyanide decomposes and a small quantity of antimony is precipitated with the tin ferrocyanide; precipitation in the cold is slow and the precipitate is difficult to filter off. The liquid is cooled to room temperature and the precipitate is filtered off rapidly and washed 5 times with a cold solution of 10 g. of tartaric acid and 5 ml. of 10 per cent. potassium ferrocyanide solution in 200 ml. of water.

Determination of Antimony.—The filtrate is diluted to 400 ml. and treated with hydrogen sulphide first in the cold (for about 20 minutes) and then after slight warming (the temperature must not exceed 60° C.). The precipitate of antimony trisulphide is filtered off, washed with cold water containing sulphuric acid and saturated with hydrogen sulphide, and rinsed with the smallest possible quantity of water into a tall 400-ml. beaker. The contents of the beaker are evaporated to dryness on a water-bath, the residue is treated with 10 ml. of conc. sulphuric acid, and the beaker is heated on a sand-bath until solution is complete and no more fumes of sulphur dioxide are evolved (30 to 40 minutes). After cooling, the liquid is diluted with 50 ml. of water, treated with 10 ml. of conc. hydrochloric acid, and finally diluted to 200 ml. with cold water. The antimony is titrated at 15° C. with $N/10$ potassium permanganate solution until a pink colour persists for a few seconds, the method of titration being that of Wassilieff and Stutzer (*Z. anal. Chem.*, 78, 97). One ml. of $N/10$ potassium permanganate solution is equivalent to 0·00601 g. of antimony.

Determination of Tin and Copper.—The ferrocyanide precipitate is transferred to a tall 200-ml. beaker with a jet of water, and the liquid is evaporated to dryness on a water-bath. If copper is not present, about 0·1 g. of copper sulphate is added to facilitate the decomposition of the organic matter. Ten ml. of conc. sulphuric acid are added, and the beaker, covered with a watch glass, is heated on the sand-bath, gently at first and then more strongly, until a brownish-yellow residue remains. After cooling, 50 ml. of water are added, the beaker is warmed until solution is complete, and the small quantity of carbonaceous matter is filtered off and washed with 10 per cent. sulphuric acid. The filtrate is treated with 10 ml. of conc. nitric acid, diluted to about 300 to 350 ml. with water, and boiled for 15 minutes. Metastannic acid is precipitated (in the presence of less acid the precipitate contains large quantities of iron formed by the decomposition of the ferrocyanide). The beaker is allowed to stand on the water-bath until the precipitate has completely subsided, after which it is separated from the hot liquid on a slow filter, washed with water containing nitric acid, dried, calcined and weighed as tin dioxide. The metastannic acid may be yellowish owing to the presence of small quantities of organic matter, but this is destroyed during the calcination. Copper is determined electrolytically in the filtrate by evaporating to 100 ml., neutralising exactly with ammonia, adding 5 ml. of nitric acid and electrolysing. The following are typical results obtained by this method:

		1	2	3
Antimony	added	0·0995	0·1110	0·0372
	found	0·0990	0·1104	0·0370
Tin	added	0·1200	0·0258	0·0850
	found	0·1208	0·0263	0·0856
Lead	added	0·2000	0·6370	—
	found	0·2015	0·6383	—
Copper	added	0·0500	—	—
	found	0·0500	—	—

E. M. P.

Determination of Platinocyanide. H. Etienne and A. de Rassenfosse. (*Bull. Soc. Chim. Belg.*, 1938, **47**, 818–822.)—The only procedure giving satisfactory results is a volumetric process based on precipitation of silver platinocyanide, $Ag_2Pt(CN)_4$. Ten g. of magnesium nitrate are dissolved in a little water in a graduated 500-ml. flask, and 50 ml. of 0·1 *N* silver nitrate solution are added. The solution of the platinocyanide is run in during agitation and the volume is adjusted. The precipitate is allowed to settle, and part of the liquid is filtered. One hundred ml. of filtrate are treated with 5 ml. of 6 *N* sulphuric acid (with barium platinocyanide, barium sulphate will be precipitated) and 10 ml. of 10 per cent. ferric alum solution, and the excess of silver is determined by titration with 0·1 *N* thiocyanate solution standardised against the silver solution under the same conditions. The addition of magnesium salt minimises adsorption of silver nitrate by the silver platinocyanide precipitate. W. R. S.

Determination of Sodium. N. Schoorl. (*Chem. Weekblad*, **1939**, **36**, 122–123.)—Some errors and points of interest connected with the use of the magnesium (or zinc) uranyl acetate method are indicated. The sodium triple salt has a solubility of approximately 5 per cent. in water, so that the reagent should be as concentrated as possible to minimise dilution from this source. The method should be regarded as one of quantitative crystallisation, rather than of quantitative precipitation, a minimum period of 1 hour (but preferably 24 hours) at a specified temperature (*e.g.* 20° C.) being necessary. An advantage is that the weight of the reaction-product is 65 or 67 times that of the sodium present (according as the magnesium or zinc salt is used, respectively). There is some doubt concerning the quantity of water of crystallisation associated with the final precipitate, because this cannot be removed completely at 110° C. Determinations made after heating for 24 hours at 80° C. in a vacuum, in a Pregl desiccator, enabled a constant weight to be obtained corresponding with between 6 and 7 H_2O. On exposure to air the precipitate assumed a moisture-content which depended on the humidity of the atmosphere. Thus, figures of 6·14 and 6·17 H_2O were obtained at zero humidity, and 6·78 and 6·80 at 98 per cent. relative humidity by Blanchetière and Kolthoff, respectively. In Kahane's method, the precipitation is carried out in 45 per cent. (vol.) alcohol, since it is claimed that this lowers the solubility and increases the rate of crystallisation of the precipitate. Under these conditions the Pregl desiccator method gives a value corresponding with 8·6 H_2O, although part of this may be due to alcohol of crystallisation. The method tends to give low results, but the error is small (not exceeding 3 mg. on a theoretical weight of precipitate of 264 mg.), when 10 ml. of reagent are added to a solution of not more than 10 mg. of sodium chloride in 1 ml. of water. If a solution of the sodium chloride in 10 ml. of 45 per cent. alcohol is treated with 10 ml. of reagent, the minimum and maximum errors are 0·5 and 10 mg. for the precipitates from 2 and 10 mg. of sodium chloride, respectively. These data may be used as correction factors, and the author has also obtained similar correction data (not reproduced in the paper) for the effects of solubility, adsorption and occlusion. J. G.

Detection of Nitric Acid. R. Lantz. (*Bull. Soc. Chim.*, 1939, **6**, 279–280.)—The solution of asymmetric phenyl- or β-naphthyl-imino-8-dinaphthoxazine in strong sulphuric acid is violet, and the colour changes to green upon addition of a minute quantity of nitric acid. A drop of the sulphuric acid solution to be tested is placed on a porcelain plate near a drop of reagent (0·2 g. of the dye in 1000 g. of 93 per cent. sulphuric acid) and the two drops are cautiously mixed, the unknown being added to the reagent. As little as 0·005 per cent. by weight of nitric acid in sulphuric acid gives a decided reaction. If the reagent is diluted with sulphuric acid to one-tenth of the above concentration, a tenfold sensitiveness may be obtained. Nitric acid can thus be detected in aqueous solutions if these are gradually added to a large excess of reagent. W. R. S.

Determination of Nitrous Acid (as N_2O_3) in Sulphuric Acid. V. N. Zimarez. (*Zav. Lab.*, 1938, **7**, 555–557.)—The permanganate method is unsatisfactory for Glover acid (*cf.* Pieters and Manners, *Z. anal. Chem.*, 1930, **82**, 218–224; Abst., ANALYST, 1931, **56**, 65), and the standard Russian method for this acid is also not satisfactory. The following modification of the latter is proposed:—*Reagents.*—*Standard sodium nitrite solution*, equivalent to 0·01 mg. of N_2O_3 per ml. An aqueous solution of 0·1816 g. of pure sodium nitrite is made up to 1 litre and 10 ml. are diluted to 100 ml. to form the standard solution. *Griess reagent.*—(A) A solution of 0·1 g. of α-naphthylamine in 6 ml. of 80 per cent. acetic acid is made up to 100 ml. with water; it is kept in the dark. (B) Ten mg. of sulphanilic acid are dissolved in 100 ml. of water. For the analysis, equal volumes of (A) and (B) are mixed. The mixed solution must be kept in the dark and for not more than 24 hours. *Sodium acetate solution.*—25 g. of crystalline sodium acetate per 100 ml. of water. *Acetic acid*, 60 to 80 per cent. *Method.*—Ten ml. of the acid to be tested are added to water in a graduated flask, care being taken to avoid loss of N_2O_3 through heating of the liquid, and made up to 100 ml. Two to three ml. of sodium acetate, 2 ml. of acetic acid, 5 ml. of the Griess reagent, and 1 ml. of the standard solution of N_2O_3, are introduced into a Nessler cylinder, with a side-tubulure, containing 20 ml. of water, and into a second cylinder are introduced 20 ml. of water, 5 ml. of sodium acetate solution, 5 ml. of the Griess reagent, 1 ml. of the diluted acid under examination, and 10 ml. of acetic acid. The solutions are stirred with glass rods, allowed to stand for 15 to 20 minutes, diluted with water to 80 ml. and again stirred. The colours are compared by looking vertically downwards, and the liquid with the deeper colour is diluted to 100 ml., stirred again and some (not more than 70 ml.) is run off. Acetic acid (up to 2 ml.) is added, and the solution is again diluted to 100 ml. If the colour is still too deep this process is repeated, less of the solution being run off each time, until the intensities of colour in both cylinders are approximately equal. The shades are then matched by the addition of either acetic acid (which makes the tint bluer) or sodium acetate (yellower tint) to the 80 ml. in the second cylinder, the contents of which are then made up to 100 ml. The deeper solution is diluted as before, until both colours are of equal depth. Then, if *a* and *b* are the number of ml. respectively of the standard and of the tested solutions, and *d* is the density (at room temperature) of the acid analysed, the percentage of nitrous acid (calculated as the anhydride) is $\frac{a}{b \times d \times 100}$ A blue tint is preferable to a yellow for colour matching. The advantages of this method over the previous titration method of determination of the dye formed are described. Results with synthetic mixtures agreed well with those obtained by the permanganate method. With Glover acid they differed from the results of the titration method and of the permanganate method, and the authors recommend the use of this new method for such acid. E. B. D.

Potentiometric Determination of small Amounts of Bromide. S. K. Afanasev, M. A. Portnov and Yu N. Chepelkin. (*Zav. Lab.*, 1938, **7**, 547–550.) —In the manufacture of bromine by extraction from sea-water (*cf.* Stewart, *Ind. Eng. Chem.*, 1934, **26**, 361) rapid control tests are required for (*a*) determination of bromide in the original material, (*b*) determination of bromine in the air-halogen mixture after chlorination and blowing. (*a*)—Chirkov's method (*Zav. Lab.*, 1935, **4**, 402), which consists in the potentiometric titration of a small amount of sodium or potassium chloride (kept saturated by contact with the solid chloride throughout the titration), is considered best for industrial control. For the brine of the Karabougaz–Goll bay, which was examined by the authors, a correction for organic matter was required. To 100 ml. of the brine were added 5 ml. of 20 per cent. sulphuric acid and 50 g. of sodium chloride (chemically pure), and the mixture was titrated potentiometrically with a 0·03 *N* solution of hypochlorite, a platinum wire and a saturated calomel electrode being used. Tests with synthetic mixtures showed that results were not affected by the presence of magnesium sulphate nor by changes in concentration of sulphuric acid and the substitution of hydrochloric acid for it. (Time of experiment, 15 to 20 minutes.) For the correction, the theoretical volume of the hypochlorite solution and 5 ml. of 20 per cent. sulphuric acid were added to 100 ml. of brine; after 4 to 5 minutes potassium iodide was added, and the liberated iodine was titrated back with standard sodium thiosulphate solution; from the results the hypochlorite consumed by the organic matter was calculated. A blank titration was made to determine the bromide present (0·001 to 0·0015 per cent.) in the "chemically pure" sodium chloride used. Results obtained by the rapid method agreed well with those by other methods and were sufficiently accurate for a control test. The bromide ion could be determined at a concentration of 0·15 g. per litre.

(*b*)—The determination of bromine in the air-halogen mixture was effected potentiometrically after absorption. To simplify the analysis and increase its speed, absorption and reduction of the bromine were obtained simultaneously by replacing the sodium carbonate solution by a 1 per cent. solution of sodium bisulphite. The solution was titrated potentiometrically with $N/10$ silver nitrate solution. The indicator electrodes was a silver spiral (diameter 1 mm.) in a saturated solution of calomel. Satisfactory results were obtained with test solutions. The sudden increase of potential was well-defined only when the ratio Br'/Cl' was greater than 1, but by a method of parallel lines (described by Chirkov) titration curves which were sufficiently accurate could be obtained with other ratios. The chlorine could also be determined simultaneously by this method, from a second sudden rise of potential. Excessive dilution of the solution titrated must be avoided. (Time of titration, approximately 20 minutes. Relative error, 1·3 per cent.) E. B. D.

Determination of the Salts in Cyanide Flux. A. A. Korinski. (*Zav. Lab.*, 1938, **7**, 550–554.)—The equation for the formation of cyanide flux or crude cyanide is:—$Ca(CN)_2 + 2NaCl \rightleftharpoons 2NaCN + CaCl_2$. For the control determination of the four compounds a method has been worked out based on the solubility of the two sodium salts and the insolubility of the calcium salts in liquid ammonia. The total sodium is determined in an aqueous solution of the flux by the zinc uranium acetate method; the total chloride and cyanide are also determined. Approximately 2 to 3 g. (unweighed) of the flux are then powdered coarsely and shaken with about 200 ml. of liquid ammonia (previously dehydrated by passing the vapour over solid caustic potash), in a conical flask in the stopper of which a calcium chloride tube containing solid caustic potash is fitted. After standing for 15 to 20 minutes, with shaking at intervals, the solution is filtered into a conical flask with side-tube (a vacuum flask is too thick to stand the cold ammonia). The side-tube is connected with a Drechsel flask in which are 25 to 30 ml. of $N/10$ silver nitrate solution. The filter is covered with a glass plate in which a hole, 2 mm. in diameter, permits ammonia fumes to escape. When 30 to 40 ml. have been filtered the funnel is replaced by a tight-fitting stopper. After the ammonia fumes have evaporated into the silver nitrate solution (in 1 to 1½ hours), the residue is dissolved in 100 to 120 ml. of water, the solution is shaken, and the cyanide is determined in 20 ml. by the Liebig method and the chloride by the Volhard method. From the ratio CN'/Cl' and the amount of total sodium the percentages of sodium cyanide and chloride can be found. From these results and from the known total cyanide and chloride the calcium cyanide and chloride can also be found. Preliminary experiments with synthetic mixtures had shown that in direct determination of the chloride and cyanide combined with sodium, some double decomposition occurred, probably through absorption of moisture from air during filtration and washing of the residue with ammonia. The shortening of the method by the determination of a ratio only, and the improvement in the apparatus, are therefore important. Test analyses with synthetic mixtures yielded results sufficiently accurate for a commercial control test. Thus, for one sample, results were:—NaCN, theory 41·52 per cent., found 41·66 per cent.; NaCl, theory nil, found 0·55 per cent.; $Ca(CN)_2$, theory and found, nil; $CaCl_2$, theory 56·13 per cent., found 56·20 per cent. In the commercial fluxes analysed only very small amounts (approximately 1 per cent.) of sodium chloride occurred, practically all the chloride being present as calcium chloride; both cyanides were present. Further experiments with many different samples of fluxes are required before a general statement can be made as to their composition. E. B. D.

Microchemical

Simplified Combustion Tube-Filling for Micro Carbon and Hydrogen Determinations. J. B. Niederl and V. Niederl. (*Mikrochem.*, 1939, 26, 28.)—Lead chromate may be omitted from the combustion tube filling without any decrease in the accuracy of results in the determination of compounds containing sulphur. The metallic silver in the filling, at a temperature of 400° C. and above appears to be able to absorb quantitatively the oxides of sulphur. J. W. M.

Modifications of Pregl's Micro Carbon and Hydrogen Determination in Humid Tropical Atmospheres. M. C. Nath. (*Mikrochem.*, 1939, 26, 165–169.)—Too low percentages of carbon were always obtained by the Pregl micro-combustion method during the summer in India. By using the following precautions accurate results may be obtained: the combustion time is increased from 10 to 15 minutes; the air and oxygen are drawn through at a rate of 4 to 5 ml. per minute; the rubber connection between the combustion tube and the calcium chloride tube is changed after each combustion. The other rubber connections between the absorption tubes are changed after three combustions. Immediately after being disconnected the absorption train is capped and transferred to the balance room where the humidity is kept constant. Two blank experiments are carried out, one just preceding and the other following the analysis of the substance, and the mean is taken, to avoid errors due to change in atmospheric conditions.
J. W. M.

Detection and Estimation of Silver on Impregnated Filter-paper. N. D. Costeanu. (*Mikrochem.*, 1939, 26, 170–174.)—Reagent papers are prepared by impregnation with a saturated solution of a suitable substance, and allowed to dry in the air. The following substances give a black or coloured stain in the pores of the paper with silver nitrate solutions: ferric ammonium citrate, hydroquinone, pyrogallol and tannin in aqueous solutions, phenylhydrazine and gallic acid in alcoholic solutions, formaldehyde, gum arabic, starch and protein in alkaline solutions, chloral in ammoniacal solution, boric acid in acetic acid solution, sodium bisulphite and potassium dichromate. Of these, the following are most suitable: ferric ammonium citrate, phenylhydrazine, hydroquinone and formaldehyde. Standard papers are prepared by dropping equal-sized drops (0·25 c.mm.) of a series of standard silver nitrate solutions on to the papers impregnated with the reagent and dried. The standard solutions contain 1 mg., 0·5 mg., 0·1 mg., 0·05 mg., and 0·01 mg. of silver per ml., respectively. The weakest solution that will just give a stain on the papers contains 0·01 mg. of silver per ml., which, in a drop of 0·25 c.mm., implies a *limit of identification* of 0·0025γ of silver. For the estimation the silver is separated from other elements and converted into nitrate, and the solution is diluted to a known volume. A drop is transferred to the reagent paper, and the size and intensity of the fleck are compared with those on the comparison paper impregnated with the same reducing substance. The amount of silver present may then be calculated. The method is very useful for determining the silver-content of jewellery, medals and objects of art, as a sample may be taken without damaging the object. Photographs are given of 10 comparison papers. J. W. M.

Spot Test for Iron and Uranium. E. A. Kocsis. (*Mikrochem.*, 1938, **25**, 13–15.)—Quercetin and quercitrin (Schuchardt, Gönlitz) are used as reagents for iron and uranium. A drop of the test solution is placed on filter-paper (Schleicher-Schüll, No. 589), and before it is dry a drop of a 0·2 per cent. alcoholic solution of the reagent is added. After a few seconds an olive-green colour appears in presence of iron or a rust-brown colour in presence of uranium. Strong acids and coloured cations interfere with the test. Quercetin and quercitrin also react with arsenates, arsenites, cupric and zinc compounds and ammonia, giving bright yellow colours. The limit of identification for iron in the test is 0·3γ and for uranium 3γ. Ferrous and ferric ions react similarly. The reaction may be applied conversely to detect quercetin or quercitrin, uranyl nitrate being used as reagent; the limit of identification is 3γ. J. W. M.

Microscopical Detection of Rubidium in Presence of Caesium. H. A. Frediani and L. Gamble. (*Mikrochem.*, 1939, **26**, 25–27.)—Naphthol-yellow-S (potassium salt of 2·4-dinitro-α-naphthol-7-sulphonic acid), as 0·5 per cent. aqueous solution, is used as reagent. It gives a yellow precipitate with solutions of potassium or rubidium salts, but not with those of other alkali metals. Its effect on other metals was tested by mixing a drop (0·04 ml.) of the reagent with a drop of solutions containing the following ions at a concentration of 40 mg. per ml.:—sodium, lithium, ammonium, caesium, magnesium, thallous, silver, lead, bismuth, cupric, mercuric, stannic, zirconium, ferric, and cobalt. Of these, only the following gave precipitates:—silver, lead, cupric, mercuric, thallous, and stannic; these would ordinarily be removed before testing for the alkali metals. Potassium alone among the alkali metals reacts similarly to rubidium. Small amounts of free, strong acids prevent the formation of the rubidium salt; strong acids are therefore neutralised with sodium hydroxide (free from potassium and rubidium) before the test. Acetic and formic acids do not interfere. The concentration limit of the test for rubidium is 3·0 mg. per ml.; at this concentration yellow needles are formed immediately on mixing a drop of the solution with a drop of the reagent. The extinction angle is 76·4° in polarised light. The limit of identification, determined by the method of Benedetti-Pichler, is 6·8γ. J. W. M.

Reviews

LABORATORY MANUAL OF ORGANIC CHEMISTRY. By HARRY L. FISHER, Ph.D. Fourth Edition. Pp. xxiii + 412. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 13s. 6d. net.

Those familiar with the famous practical text-books of Cohen, Sudborough and James, and Gattermann will be amazed on opening Fisher's Laboratory Manual to find an almost complete absence of formulae, equations and explanations, and so, perhaps, become possessed with a fear, fortunately not justified, that the volume under consideration is a mere "cookery" book. Further investigation, however, reveals many merits.

In Part I seventy-seven "laboratory experiments" are described. The first thirty-eight pages are devoted to boiling-point and melting-point determinations, together with a very full discussion of matters relevant to these topics. In particular the author recommends the recording of corrected values, and to this end urges standardisation of thermometers, or, better still, the use of short-range thermometers of his own design (which are similar to the well-known Anschütz type). The determination of molecular weights by Rast's Camphor Method is described in detail, and several substances suitable for the replacement of camphor are given. Mention is also made of the dual value of "K" according as the method is used on the macro- or micro-scale, but the fact that it varies for each observer seems to be overlooked.

The actual preparations are very varied, but seem to have no obviously logical sequence; thus a preparation involving a Grignard reagent precedes the preparation of ether (Expts. 13 and 14). Among the more unusual preparations may be mentioned Monastral Blue, Tyrian Purple, a synthesis of camphor, an example of the Diels–Alder reaction and the reagents dimethyl-glyoxime, dithizone and tetramethyl-base.

The arrangement of each preparation is reminiscent of "Organic Syntheses." Thus precise directions are followed, where necessary, by a set of notes and references. In place of the usual equations and explanations are numerous questions, which require considerable reading on the part of the student before satisfactory answers can be compiled. In many instances the student is helped by a list of references to such standard works as Cohen's *Organic Chemistry for Advanced Students*, Stewart's *Recent Advances* and Gilman's *Organic Chemistry*. Various journals are also referred to.

Part II is devoted to organic combustions and opens with an historical survey of considerable interest; a valuable discussion of weighing is also included. The methods recommended involve several modifications, of the author's own invention. As far as can be judged, without actual test, these modifications are quite sound and make for accuracy. Magnesium perchlorate is used as an absorbent for water, and the use of palladous chloride solution (a detector of carbon monoxide) is suggested as a check against incomplete combustion. The author, on the grounds of "no first-hand experience," omits all reference to micro- and semimicro-methods. The determination of nitrogen is treated in great detail and a method using a manometer is minutely described. The determination of halogens, sulphur and phosphorus is, by contrast, very brief and somewhat disappointing.

Throughout the book there is evidence of practical experience, care and accuracy. Only one trifling error has been noticed: the melting-point of 2:4-dinitrophenol is not 12·8° C. (p. 160). Any student who works through this book, faithfully doing the *implied* reading and then answering the questions, will certainly have laid the foundation of a claim to the title of organic chemist. Dr. Fisher's book, though a departure from the orthodox, rightly used, is excellent.

HAROLD TOMS

TASCHENBUCH FÜR DIE LEBENSMITTELCHEMIE. By A. THIEL, R. STROHECKER and H. PATZSCH. Pp. xi + 173. Berlin: Walter de Gruyter & Co. Price RM.8.60.

This book contains a collection of tables for the use of those engaged in the chemistry of food products.

The tables, 66 in number, are in 7 sections dealing respectively with Milk, Water, Alcohol, Sugars, Wine, Fats and General Analysis. Several of the tables, especially those in the last-named section, are available in most handbooks of this type, and include hydrometer tables, tables giving densities of aqueous solutions of common acids and alkalis, densities of sugar solutions, physical and chemical constants of fats and oils, densities of alcohol-water mixtures, and so forth. Many of the tables, however, have been taken from comparatively recently published German journals and are for use in connection with special methods of analysis: for example, with Grossfeld's method for determination of the amounts of butter-fat and coconut oil in fat mixtures from the "A" and "B" values; Fincke's method for the polarimetric determination of sugars in chocolate; Tilmans and Luckenbach's method for determining the extent of neutralisation of milk.

The source of each table is given and in a few instances a summary of the method of determination and use of the table is included, but usually it would be necessary to refer to the original paper for details.

The book is well printed and the tables are clearly set out, determined values being printed in red, the values sought in black. A bibliography of relevant literature is given.

For anyone regularly using these German methods of analysis this book would be very useful. The general information provided is, however, very limited compared with that given in the well-known handbooks.

M. SHAW

NEWER METHODS OF VOLUMETRIC CHEMICAL ANALYSIS. Editor: WILHELM BÖTTGER. Pp. 268. London: Chapman & Hall, Ltd. 1938. Price 18s. 6d.

Text-books covering a wide field frequently tell us all too little about points of special interest. The present book is different, for it deals only with a limited number of processes and goes into them very fully. The work, which is an American translation by R. E. Oesper from the German, is a collection of seven monographs by authors the names of some of whom are well known in this country in connection with the subjects on which they write. The contributions are: (I) The Elimination of the Titration Error in Acidimetric and Alkalimetric Titrations, by E. Brennecke (Fresenius Chemical Laboratory, Wiesbaden, Germany), 20 pp.; (II) Ceric Sulphate as Volumetric Oxidising Agent, by N. H. Furman (Princetown University, U.S.A.), 21 pp.; (III) Alkaline Permanganate as Volumetric Oxidising Agent, by H. Stamm (University of Halle, Germany), 9 pp.; (IV) Iodate and Bromate Methods, by R. Lang (Technical High School, Brünn, Czechoslovakia), 52 pp.; (V) Chromous Solutions as Volumetric Reducing Agents, by E. Brennecke, 19 pp.; (VI) Oxidation-reduction Indicators, by E. Brennecke, 37 pp.; (VII) Adsorption Indicators for Precipitation Titrations, by K. Fajans (University of Michigan, U.S.A.), 48 pp.

The object of the editor was to obtain from the various writers as uniform as possible a mode of presentation which would bring out (*a*) the fundamental basis of the processes, and (*b*) practical directions for carrying them out. The proportions of (*a*) and (*b*) vary appreciably in the different contributions, but the approach has been mainly from the practical angle, and the theoretical treatment is non-mathematical.

In the first contribution the effect, on the change-point of indicators, of temperature, concentration of salts, presence of carbon dioxide, and so on, is clearly discussed and methods for eliminating or correcting for these factors in accurate work are described. In one example given, methyl yellow is advocated for the titration of sodium carbonate with hydrochloric acid; the titration should be carried out to a standard shade by matching with a solution containing suitable coloured inorganic salts; the indicator correction is obtained by titration of a solution containing the same amount of sodium chloride as that formed in the first titration; carbon dioxide must be removed by boiling (the solution being afterwards cooled) as the acid character of carbon dioxide is considerably increased in the presence of salts. The chapter on ceric sulphate gives an excellent practical account of the uses of this volumetric oxidising agent in the determination of various metals and organic substances.

The section on alkaline permanganate is in the nature of an original contribution on a method developed by the writer himself, and applicable mainly to the determination of organic compounds. The principle is that the oxidation of the material being determined involves the rapid partial reduction of the permanganate to manganate, the slower further reduction of manganate to hydrated manganese dioxide not being allowed to occur; the excess permanganate is subsequently titrated back with a suitable reducing agent. The action of the permanganate under the conditions laid down is said to be specific, oxidation occurring when the compound contains an aliphatic carbon double bond, an alcoholic or phenolic hydroxy group or amino or carbonyl group, but not when it has only carboxylic, sulphonic, nitro, alkyl, halogen or ethereal oxygen groupings. Among the substances readily determined by this method are: hypophosphite, phosphite, iodide, iodate, cyanide, methanol, formaldehyde, glycol, glycerol, pentoses, hexoses, salicyclic acid and phenols; chloride, bromide and benzoic and toluic acids consume no oxygen and do not interfere.

Iodate and bromate methods reviewed in the fourth section have been found applicable to the determination of a large number of metals and organic compounds. The familiar iodate method of Andrews is exhaustively discussed together with the newer iodine cyanide and iodo-acetone methods. The description of the György method and its modifications for the bromate titration of antimony in hydrochloric acid solution with methyl orange as indicator recalled to the reviewer that he had some time ago found that it was necessary to keep the hydrochloric acid concentration down to about 10 to 15 per cent. strength in order to secure sharp end-points and accurate results. It is interesting to note from this book that German work, carried out much earlier and apparently generally overlooked in this country, pointed to a similar conclusion.

The treatment of oxidation-reduction indicators is one of the best from the practical point of view that has yet appeared. Professor Fajan's contribution on adsorption indicators deals principally with the fundamental aspects and gives less analytical detail than most of the other authors' sections. The value of the book is enhanced by the comprehensive bibliographies which supplement the sections, and by an index.

From the standpoint of analytical practice, a method of determination is often only the last stage of a process, and it will be understood that for preliminary separations, where necessary, reference would generally have to be made elsewhere. Whilst the book can thus be looked on as an adjunct to existing text-books on quantitative analysis, it is one for which a need has existed, and the collection of the available information in the present convenient form will be widely appreciated.

S. G. CLARKE

WEEDS, WEEDS, WEEDS. By SIR CHARLES V. BOYS, LL.D., F.R.S. Pp. 113. 2nd Ed. London: Whitman & Co., Ltd. 1938. Price 2s.

It must not be surmised that the appearance of the second edition of this work so soon after that of the first indicates that remedies suggested for weed eradication have not been as effective as the author avowed; it means that a still wider public requires the work. On the seventieth and final page of the first edition Sir Charles said "adieu" to all his "gentle readers," but on the last and one hundred-and-tenth page of the present volume there is no such farewell. It may be fair, therefore, to presume that soon we may expect a large and authoritative work on weed eradication by the author, embodying the results obtained by the application of his scientific knowledge to the problem. There is a suggestion that this last volume results from talks with readers gathered under an apple tree on the author's lawn. The talks were only imaginative. Anyone standing on that lawn would surely place Professor Boys under suspicion until a survey of the lawn (and of the surrounding garden) had been made. What a sense of guilt would be experienced if a daisy were descried, even if the explanation were given that it was of the kind that had the habit of popping up in a single night! Can it be that the author has lost a little confidence, because he now states that certain remedies may have a successful action only if they are applied to weeds on particular soils? Be that as it may, the book now deals with theory and explains the action of both wetting agents and plant poisons, and it gives further information relative to the application of the well-known weedicides. There is one method of weed eradication that perhaps it is not the purpose of the book to stress, and that is by digging. It may be that this is not done in the best weed-killing circles. Undoubtedly, a scientific superiority is experienced when a friend is informed that a nettle that once grew under a favourite apple tree was completely annihilated by cutting its stem and placing a drop of a concentrated solution of sodium chlorate on the bleeding stump. But a large amount of jubilation could have been experienced had the said nettle been lifted with a fork and then carried with suitable incantations to the kitchen stove. Under such conditions there is truly no resurrection.

Much information is contained in the recently published edition, and the expenditure of 2s. would always be justified if only to get the atmosphere, once more, of Sir Charles's individuality. F. W. F. ARNAUD

BACTERIAL METABOLISM. By MARJORIE STEPHENSON, Sc.D. Pp. xi + 391. London: Longmans, Green & Co. 1939. Price 21s. net.

This advanced text-book is the outcome of a monograph by the same author in the "Series of Monographs on Biochemistry" published in 1930. The book has, however, been entirely re-written and the new work of the past nine years has been incorporated, the subject having far outgrown the scope of a monograph. The aim of the work is to choose from the mass of data on the chemical reactions brought about by bacteria those facts that throw light on the essential chemical processes accompanying bacterial life. The author aptly compares the study of bacterial metabolism with an endeavour to gain an idea of the life of a household by observing the kind of articles daily imported by the various tradespeople and by a scrutiny of their ash bins. The headings of the chapters are as follows:—Introduction; Respiration; Polysaccharides; The Fermentation of Hexoses; The Decomposition of Proteins; The Metabolism of Nucleic Acid; Nutrition and Growth; Nitrogen Fixation; Autotrophic Bacteria; Bacterial Photosynthesis; Enzyme Variation and Adaptation. These are followed by an appendix, a bibliography and author and subject indexes. It is only possible in review to give a brief outline of the scope of some of these chapters. The introduction outlines the historical development of knowledge of bacterial metabolism up to the discovery of the enzyme zymase by Buchner, and proceeds to the consideration of energy relations of organisms to their substrates. It is shown on experimental evidence that with mould growth the formation of mould from substrate involves an expenditure of energy apart altogether from energy lost in respiration, and the requirement of energy for "maintenance" is discussed.

The subject of "Respiration"—used to denote any chemical process, aerobic or anaerobic, by which energy is liberated by the cell—is fully dealt with. The use of the methylene blue technique in the study of the catalytic transfer of hydrogen is described and the use of other oxidation-reduction indicators. Here we learn about the dehydrogenase enzymes, and the necessity of a "carrier" for the transfer by these enzymes of organic hydrogen to atmospheric oxygen; about cytochrome, its spectrum, which represents three haemochromogen-like substances, and its function as an oxygen "carrier"; about flavoprotein and co-enzymes I and II, peroxidase and catalase, glutathione and its function in the oxidation of protein; about anaerobic respiration, oxidation and reduction potential, redox indicators and their capacity to function as reversible hydrogen and oxygen "carriers"; about anaerobic mechanisms for obtaining energy, in which by their enzymes organisms growing anaerobically use organic compounds as hydrogen donators and acceptors; and about "dismutations" in which similar molecules play the parts both of donator and acceptor.

The chapter on the polysaccharides deals with the breakdown of cellulose, starch, hemicelluloses, pectins, and so forth, and with the nature of gums and slimes. It is interesting to note that an organism has been isolated from the gum acacia tree which can produce a gum identical in character with true gum acacia, when grown on potato juice with 5 per cent. of cane sugar and 0·5 per cent. of tannic acid. The immunological importance of the polysaccharides of the capsules of pneumococci and *V. cholerae* is dealt with here.

The chapter on the fermentation of the hexoses opens with an account of recent knowledge concerning the transformations of the hexose molecule into carbon dioxide and alcohol by means of brewer's yeast. This molecule is shown to be transformed into no less than 14 intermediate compounds by means of a very complicated system of enzymes and carriers in which glycerophosphates and phosphoglyceric acids play a prominent part. Lactose fermentation by different bacteria follows, and glucose fermentation, an account being given of the formation of acetyl-methyl-carbinol, succinic, lactic, propionic, acetic and formic acids, and acetone. This chapter includes accounts of the fermentation of 3-carbon and 4-carbon compounds.

The chapter on the decomposition of the proteins deals first with the bacterial proteases which split the protein molecule to the amino acid stage, then with the mechanism of the breakdown of the amino acids which seems to be more intimately bound up with the cell structure. Nine types of such breakdown are discussed, such as "decarboxylation with formation of the amine" and "anaerobic breakdown with production of hydrogen," and there follows a table setting out the various amino acids, the class of breakdown, and the organisms which have been observed to effect it. The breakdown of tryptophane is given special treatment, as is also the production of indole and skatole. The chapter on nutrition and growth is of special interest; it includes some of the researches of Fildes, Knight, Koser and Rettger, and deals with the requirements of bacteria ranging from those that can synthesise all their amino acids from glycerol and ammonium phosphate to those requiring a formidable list of amino acids and vitamins. In the chapter on the autotrophic bacteria one finds a good account of these very remarkable micro-organisms and of the way in which they obtain the energy necessary for the metabolism by inorganic oxidations of ammonia, nitrites, sulphur and sulphur compounds, atmospheric hydrogen, and carbon monoxide and by oxidations of the very simple organic compounds, formic acid, formaldehyde and methane, of the way in which some can tolerate such an extremely acid *p*H as 0·6, and of the inhibitory effect, upon the growth of the nitrobacter, of the addition of organic compounds. The chapter on bacterial photosynthesis describes the work of Van Niel on the purple and green sulphur bacteria and that of Muller and Graffon on the purple bacteria and shows how these curious micro-organisms depend on carbon dioxide for their supply of carbon and upon solar radiation for their energy, and that the pigments they contain are closely related to, but not identical with, chlorophyll.

The book is very well written, for the author has a complete mastery of this extremely difficult and comprehensive subject together with a free and unhampered style. If there is anything to be desired it is perhaps some sort of summary—chapter by chapter, or a summary of contents at the heading of each chapter, to assist the infirmities of the reader.

The book has a good index and a very good bibliography; it is well compiled and the subject-matter well arranged. The paper and type are excellent, and as an advanced text-book on the subject the work can be strongly recommended.

D. R. Wood

MAY, 1939 Vol. 64, No. 758

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on April 5th, 1939, the President, Professor W. H. Roberts, in the chair.

The following were elected members of the Society:—H. A. Frediani, Ph.D., B.A., M.S.; B. S. Platt, Ph.D., M.B., Ch.B.

Certificates were read in favour of the following candidates for Membership:—J. B. Firth, D.Sc., M.I.Chem.E., F.I.C.; G. Isles; C. H. Wordsworth, B.Sc., A.I.C.

The following three papers were presented and discussed:—"Food Inspection and Analysis in Holland," by J. Straub, Chem.Ing.; "The Determination of Traces of Zinc in Biological Material and Natural Waters," by N. L. Allport, F.I.C., and C. D. B. Moon, A.I.C.; "The Evaluation of Hydrogen Peroxide," by S. M. L. Tritton, M.P.S., F.I.C.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Leeds on March 25th, 1939. The Chairman (Professor T. P. Hilditch) presided over an attendance of thirty-one.

The following papers were read and discussed:—"Silicosis and the Analyst," by F. S. Fowweather, M.Sc., F.I.C., M.D., M.R.C.P., D.P.H.; "Some Notes on the Examination of Paraldehyde," by A. R. Tankard, F.I.C., D. J. T. Bagnall, A.C.G.F.C., F.I.C., and A. Smith, B.Sc., F.I.C.; "An Improved Table for use with British Standard Specification Density Hydrometers for Milk, B.S.S. No. 734, 1937," by J. G. Lunt, B.Sc., F.I.C.

A resolution of appreciation of the late E. R. Bolton, and of condolence with Mrs. Bolton, was passed unanimously.

Deaths

With deep regret we record the deaths of:

Richard Augustus Cripps, Member of Council, 1910–11.
Henry Francis Everard Hulton, Member of Council, 1923–24.

Obituary

EDWARD RICHARDS BOLTON

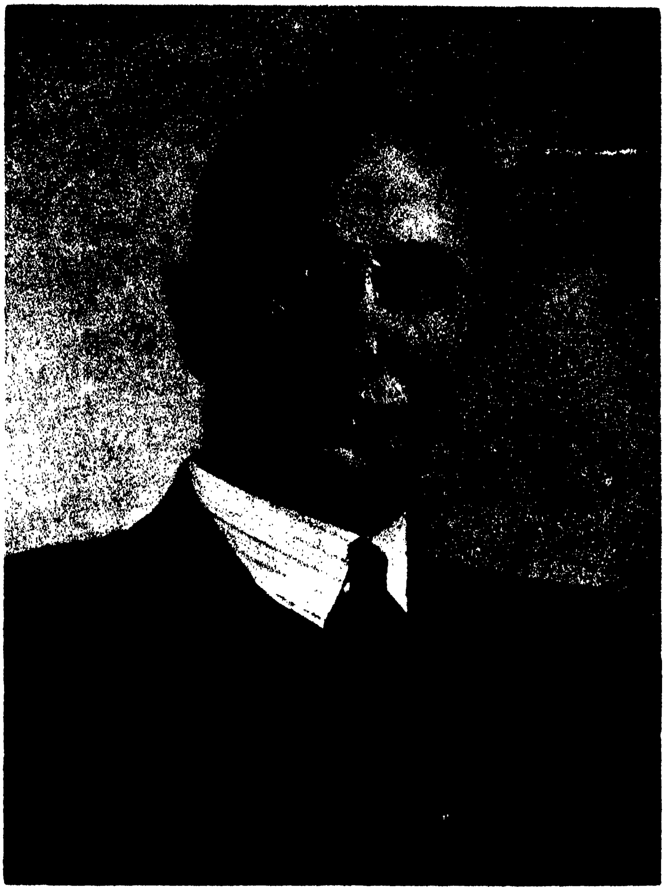
Bolton was born in 1878 at Blackrock, Co. Dublin, and was the only son of J. A. Bolton; there is a long record of Boltons in counties Dublin and Wexford. His school was Bedford (Elstow), and he studied chemistry at King's College, London, 1896 to 1897, and then in Fresenius's laboratory, Wiesbaden. His first appointment was in Newcastle, in heavy chemical industry, and in 1902 he came to London as chemist to the East Indian Products Co., Ltd., at the Albert Oil Mills, Hammersmith (later merged with Loders & Nucoline, Ltd.). It was at these mills that Bolton essayed, and successfully, the first commercial caustic refining of coconut oil in this country. He became a director of the firm, having in the meantime started in analytical and consulting practice in Hammersmith. The early part of this century saw a great development in the oil and fat industry; to this Bolton in no small measure contributed, and its great importance became obvious to all during the difficult war years.

In 1920 Technical Research Works, Ltd., was founded, with premises at Milner Street, London, S.W., Bolton being managing director and transferring his own private laboratories to the same address. This year was eventful in that it is the date of Bolton's patent for the continuous hydrogenation of unsaturated oils, fats and the like, and from Milner Street hydrogenation plants went to many countries. Technical Research Works eventually passed into Bolton's sole control.

Bolton early became an authority on the analysis and technology of oils and fats; this industry and a number of food industries were his main field. In the actual control of industries he was a director of several companies, and for five years was chairman of Bladen Dairies, Ltd. He was analyst, consultant and technical adviser, research worker and inventor, expert witness, business man and author; in all he excelled.

He joined the Society in 1905, and was Member of Council 1911 to 1912. In 1915 he became Honorary Secretary, and after ten years' devoted service in that office he increased the Society's debt to him during a distinguished Presidency in 1926 and 1927; thereafter he served as Past President on the Council. Thus for 24 years he was continuously in office and worked indefatigably, and most effectively, for the good of the Society and for the causes which it has at heart.

In analytical chemistry Bolton did much original work. This was published mainly in The Analyst. His first paper, on ghee, was published in 1910, in association with C. Revis; the last two, in collaboration with K. A. Williams, were concerned with whale oil and appeared in 1938. Between these were numerous papers, all of value, and many of outstanding importance. In the last few years one remembers particularly how he delighted us with his demonstration of the colour measurement of opaque surfaces with the Bolton and Williams Photoelectric Colorimeter. At the monthly meetings of the Society in London his contributions to the discussions on the work and papers of others will be sadly missed. In 1911 there appeared the famous *Fatty Foods* (Bolton and Revis), followed by a second edition, *Oils, Fats and Fatty Foods* (Bolton) in 1928. In



From a photograph by E. R. Bolton

Emery Walker Ltd. ph. sc.

E. L. Bolton

these books he gave fully of his genius and his wide experience; there has been no book more satisfying to the analyst. He was also the author, with R. G. Pelly, of *The Resources of the Empire: Oils, Fats, Waxes and Resins.*

Bolton's knowledge of fatty oils and oil-seeds led to a demand for his services on many bodies and committees, and the demand was generously met. He was a member of the Committee of Analysts, Ministry of Food, Oils and Fats Branch, in 1918; Chairman of the Oils and Oil-seeds Committee and of the Tung Oil Sub-committee, and member of the Plant and Animal Products Committee, Imperial Institute; Fertilisers and Feeding Stuffs required him as a member of the Departmental Committee to draft the Act of 1926, and subsequently as a member of the Statutory Advisory Committee established by the Act; he was British representative on the Commission Internationale pour l'Étude des Matières Grasses, and Chairman of the International Congress when it met in London in 1935. The British Standards Institution called him to their Chemical Divisional Council, as Chairman of two Committees and member of others. He was a member of the Panel of Analysts established by the London Oil and Tallow Trades Association; a member of the Pharmaceutical Chemistry Sub-committee, British Pharmacopoeia, 1932. In a less specialised field he had been Vice-President of the Institute of Chemistry, Chairman of the London Section of the Institute of Chemistry and Hon. Treasurer of the Federal Council for Chemistry and, more recently, a member of the British Council for Chemistry of the Royal Society; he was a Royal Institution Visitor and a member of the Delegacy of King's College, London, and was elected a Fellow of the College in 1938. He had long taken an active part in the work of the Publication Committee of the Society; he also served throughout on the Milk-products Sub-committee and was a member of the Analytical Methods Committee and of the Soap Sub-committee. This year he had started work with the Society's Sub-committee on the determination of unpolymerisable matter in oils; it was, indeed, at his suggestion that this investigation was undertaken.

A recital, albeit an incomplete one, of the bodies on which he served, and to which he gave unreservedly of his knowledge and experience, is an indication of his activities and the value placed upon them. These should be formally recorded, yet they furnish but a lifeless picture of him. One would wish, were it possible, to give a picture of Bolton as he lived his busy and fruitful life, happy in his laboratory and his many interests, of his attractive gaiety, of his enterprise and courage, of his kindliness, of his bright and amusing yet unflippant talk, of his pride in his Irish descent, an inspiration alike to his staff, his colleagues and his friends. Those who knew him will continue to refer to his published work, but will also remember with gratitude much that they received from him that could be communicated neither in papers nor in books; for he gave generously from his own ideas and experience to those who went to him—and they were many—for help in the solution of some problem either of the moment or of more lasting importance.

He was a brilliant analyst; he was just as successful in the works and in consultation. It was, perhaps, his sense of proportion, added to his other gifts, that made him so successful in these spheres; may be it was partly that his career started in the works and that his analytical practice developed later; but reasons for his success need not be analysed—they are patent in his character and abilities; we should read again his views on "The Modern Analytical Chemist" in his retiring Presidential Address in 1928.

In 1902 Bolton married Norah, daughter of Robert Binning, of Glasgow. Mrs. Bolton is well known to members of the Society, for she was frequently at the social gatherings of chemists; there are many who will retain pleasant memories of the delightful welcome they received from Mrs. Bolton and her husband at their home in Kensington. One other personal reference may perhaps be allowed; Bolton was a gifted photographer; the plate reproduction of the Society's Presidential badge, issued with THE ANALYST in April last year, was from a photograph by him, as also is the photogravure portrait in the present issue; his Christmas cards he produced himself, and they were beautiful examples of the photographer's art. Members of the Society have been at times caught unawares by his camera—the picture a delight both to Bolton and to his victim.

It seemed this year that Bolton was at the height of his powers, and that, even had he wished in the coming years to take things more easily, he would for long continue a leader in his profession. It was not to be; after a brief illness, of which even those closest to him saw not the tragic significance, he died suddenly on the evening of February 10th, 1939, to the great grief—it is no exaggeration to say to the dismay—of all who knew him. EDWARD HINKS

Stannous Chloride as a Quantitative Reagent for Selenium and Tellurium

BY W. R. SCHOELLER, PH.D., F.I.C.

JUDGING from the evidence of contemporary chemical literature, stannous chloride as a quantitative reagent for selenium and tellurium appears to be hardly used at all, and references to it are discouraging.[1] Objections are based on the fact that the two elements are not precipitated in a weighable form because they occlude the precipitant. In spite of this, I have found stannous chloride to be a most valuable adjunct of fairly general applicability in metallurgical analysis, particularly in the more usual instance of materials low in selenium and tellurium. This paper gives a brief description of a procedure which I have worked out and used for a number of years on a variety of materials. It involves nothing fundamentally novel, but the sequence of operations is original and, in my opinion, of practical value. In view of their forthcoming publication in the new edition of a book of which I am joint author,[2] I have thought it advisable to publish these notes in the form of a paper for purposes of discussion. The process will be referred to as the "stannous chloride method."

A. THE STANNOUS CHLORIDE METHOD.—The most generally applied procedure for the precipitation of selenium and tellurium in metallurgical analysis consists in saturating the solution with sulphur dioxide, a manipulation by no means free from disadvantages. The action of the gas in dilute solutions is slow, small quantities of these elements, especially tellurium, requiring protracted treatment; the precipitate is finely divided and does not settle readily. Sulphur dioxide does not reduce selenic and telluric acids. It readily reduces pure, not too dilute, solutions of the tetrachlorides, but in solutions charged with other metals (copper, iron, antimony, bismuth) interfering reactions take place. Hydrazine (used by itself or in conjunction with sulphur dioxide) is a very efficient reducing agent, but its high price discourages its lavish use. Sulphur dioxide is harmful to the respiratory passages, and the manipulation and filtration of large volumes of liquid saturated with the gas is most unpleasant.

The stannous chloride method is free from these drawbacks, the action of the reagent being immediate and stoichiometrically defined; an excess is required only to keep the solutions reduced, and time must be allowed for small precipitates to settle. Ferric chloride is unobjectionable, being reduced at the start to ferrous salt. If large amounts of copper and nitric acid are present, their interference is overcome by an essential step in the process, namely, precipitation of selenious and tellurous acids on ferric hydroxide by ammonia.[3] This step avoids destruction of nitrates by evaporation with hydrochloric acid, which is faulty in principle, as a serious loss of selenium is incurred even after addition of sodium chloride. The presence of smaller amounts of copper retained in the precipitated ferric hydroxide, far from being prejudicial, assists the precipitation of selenium and tellurium by stannous chloride, as the precipitate thus produced is not pulverulent, but flocculent; it contains copper, and is most probably cuprous selenide (telluride) formed by virtue of the reaction $SeCl_4 + 2CuCl_2 + 4SnCl_2 = Cu_2Se + 4SnCl_4$.

As for the objection that the precipitated elements occlude tin (and copper as well, if present), the essential feature of the stannous chloride process is, that it utilises this reagent merely as a convenient means for recovering the two elements in the form of a concentrate suitable for their separate determination; the washed precipitate is dissolved in strong hydrochloric acid containing bromine, and the resultant solution (which need not exceed 20 ml.) is treated with sulphur dioxide, without an intervening evaporation, for the precipitation of selenium in a pure form. The filtrate, suitably diluted, yields the tellurium upon further reduction. Hence the preliminary precipitation with stannous chloride does double duty as a concentration and purification process; the final precipitation by sulphur dioxide takes place in purer and more concentrated solution.

B. PROCEDURE.—The sequence of operations for the determination of small quantities of selenium and tellurium is as follows :

(1) *Solution.*—Whenever possible the solution is prepared with nitric acid only, preferably in a capacious flask with a funnel inserted in the neck, a flask with ground-in reflux condenser, or a Kjeldahl flask, to counteract risk of loss in the attack which is attended with more or less violent evolution of red fumes. The nitric acid should not be diluted and a large excess may be used. If the next step [B (2), below] is not applied, the acid liquid is transferred to a squat beaker for expulsion of the nitric acid by evaporation on a water-bath covered with the rings. The mass is taken barely to dryness, the residue is taken up in hot water or dilute hydrochloric acid, gently warmed if necessary to assist solution, and the insoluble residue is filtered off.

This should be examined, and tested by fusion if necessary, after drying [C (3), below].

Treatment with *aqua regia* may sometimes be required. This should be done at moderate temperature, *e.g.* on a covered water-bath or, if required, by more drastic treatment in a flask fitted with a reflux condenser (glass joint).

(2) *Precipitation with Ferric Hydroxide.*—If the material is high in copper, this step must be applied, and it is convenient also for the removal of nitric acid instead of by evaporation. The nitrate solution is diluted and treated with a suitable quantity of a solution of iron in nitric acid unless sufficient iron is already present. The quantity of iron should be 30 to 50 times that of the selenium and tellurium. The hot solution is treated with a moderate excess of ammonia, and the precipitate is allowed to settle, collected on a large filter, and washed with water containing a little ammonium chloride and hydroxide. Only if the amount of copper is very large (*e.g.* in the analysis of refined copper) is it necessary to dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation with ammonia.

(3) *Precipitation with Stannous Chloride.*—The washed iron precipitate is returned to the beaker; if its amount is small, the filter is spread against the side of the beaker, most of the precipitate is dislodged with a glass rod, and the remainder is rinsed down with hot water followed by hydrochloric acid (1 : 1). If very bulky the precipitate is scooped out of the filter, and the part adhering to the paper is dissolved in hydrochloric acid, so as to keep the volume of the solution as small as possible. The warm, fairly acid solution is stirred and treated with a freshly prepared, acid 20 per cent. solution of stannous chloride, the yellow colour of the ferric chloride being first discharged; continued addition of the reagent produces a pale reddish-brown, brown, or brownish-black colour, and, on standing, the solution is decolorised, with deposition of a reddish to black precipitate. If very little selenium or tellurium is present, the solution must be set aside overnight. The acid concentration (which may be about 1 of acid to 2 of water) in this procedure is not high enough to cause precipitation of arsenic, but should some arsenic find its way into the precipitate, it will not interfere later on. Antimony and bismuth chlorides are not reduced.

(4) *Treatment of Precipitate.*—The precipitate is collected in a funnel on a rather small pad of filter pulp lightly pressed into the apex; no filter-paper is used, hence the volume of washings can be reduced to a minimum. The precipitate is completely transferred to the filter with *N* hydrochloric acid containing stannous chloride, and washed with the same solution, and finally 2 or 3 times with 2 per cent. hydrochloric acid. The funnel is then covered with a watch-glass and the precipitate is treated with a solution of bromine in strong hydrochloric acid, added, drop by drop, through a glass tube, and the resulting solution is collected in a small conical flask (100 or 50 ml. capacity). The dropwise addition of brominated acid is continued at intervals until the precipitate has dissolved; an excess should be avoided. Finally, the filter-pad is washed with small portions of hydrochloric acid (4 acid : 1 water).

(5) *Precipitation of Selenium.*—The cold solution is cautiously treated with a very slow current of sulphur dioxide, or by dropwise addition of a solution of

sulphur dioxide in strong hydrochloric acid, until the bromine colour is discharged. As soon as this has taken place the red modification of selenium is precipitated. The gas is admitted for another 10 to 15 minutes, after which the flask is stoppered and set aside overnight or until the precipitate has coagulated. It is collected in a small porous porcelain filtration crucible, washed successively with a little strong hydrochloric acid (4:1 water) and with *N* hydrochloric acid, water, alcohol, and ether, the organic solvents being collected apart from the aqueous portion. The washed precipitate is dried for a short time at 100° C. or *in vacuo*, and the crucible is weighed, ignited, cooled, and again weighed. The loss in weight represents the selenium.

(6) *Precipitation of Tellurium.*—The filtrate and aqueous washings from the selenium are transferred to a beaker, diluted with an equal volume of water, and again treated with sulphur dioxide, or with hydrazine hydrochloride and sulphur dioxide,[4] and the tellurium is determined in the usual manner.

The percentage of tellurium is normally very much lower than that of the selenium, so that there may often be doubt as to its presence. Under such conditions I have found stannous chloride useful in detecting and recovering quantities of tellurium of the order of 0·0001 g. The filtrate from the selenium, instead of being diluted with water, is evaporated to a volume of 1 to 2 ml., which can be done with impunity, as tellurium is not volatile under these conditions. Any purple colour at this stage is due to cupric bromide. If the solution is treated with a drop or two of stannous chloride reagent, tellurium will betray its presence by a more or less pronounced brown colour. After flocculation, the precipitate of tellurium (containing Cu_2Te, if copper is present) is collected on a minute filter-pad in a very small funnel, washed twice with 2 per cent. hydrochloric acid, and dissolved in a few drops of brominated acid. The solution is collected in a 50-ml. beaker, decolorised with sulphur dioxide, and treated with hydrazine as before.

C. Practical Application.—The following are a few examples of the application of the stannous chloride method:

(1) *Selenium in Pyrites.*—This is the most common and important instance in practice; the stannous chloride method has been successfully applied to this determination for several years.

The finely powdered ore (10 to 20 g.) is treated in a 2000-ml. beaker with strong nitric acid (60 to 120 ml.). When the first violent action is over, the covered beaker is gently heated; a vigorous action must be kept up, but the heat should not be raised to the melting-point of sulphur, as the larger globules retain selenium and are difficult to attack. Finally, the clockglass is removed and the red fumes are allowed to escape. The acid is diluted with warm water, and the solution is passed through a loose filter. Should any but small particles of sulphur remain unattacked, the filter containing them must be dried, the sulphur collected, crushed, and oxidised with fuming nitric acid, and the solution added to the bulk. The warm solution (1000 to 1500 ml.) is made ammoniacal and set aside on the water-bath for a short time. The precipitate is collected on a 24-cm. filter and washed a few times with hot water, care being taken to gather the ferric hydroxide into a compact mass which is left to drain and can then be scooped out without the use of too much acid. The precipitate is dissolved in hydrochloric acid, etc., as explained under B(3).

Copper sulphide ores may be treated in the same way as pyrites.

(2) *Selenium in Stibnite, Liquated Sulphide (Crudum), and Antimony Metal.*—For this determination ammonia precipitation on ferric hydroxide is unnecessary. Five g. of the finely powdered sample are oxidised with 40 ml. of strong nitric acid; when attack is complete the beaker is uncovered and placed on a covered water-bath and the acid is evaporated just to dryness. The cold dry mass is cautiously treated with 40 ml. of hydrochloric acid (4 : 1 water) added in portions while the beaker is being kept cool. The clear solution is diluted with 50 ml. of water and cooled, and the selenium is precipitated with excess of 10 per cent. stannous chloride solution. If necessary, the precipitates from several 5-g. portions are combined. Stibnite ores may also be treated by the fusion process given under (3) below.

(3) *Selenium in Oxidised Antimony Ores.*—These are insoluble in acids and have to be opened up by fusion. Portions of 2·5 g. are fused with sodium peroxide in iron crucibles, and the fluid melts are poured out and disintegrated with water in 600-ml. beakers. The hot suspension is acidified with strong hydrochloric acid until a clear solution results; this is treated with a liberal excess of 20 per cent. stannous chloride solution. The reagent reduces hot hydrochloric acid solutions of selenic and telluric acids.

(4) *Refined Copper.*—Fifty g. of drillings are dissolved in 200 ml. of strong nitric acid added in portions, the first portion being slightly diluted. Any sulphur remaining undissolved, or any dark residue (which may contain silver selenide), must be collected and treated with fuming nitric acid. The nitrate solution is treated with a solution of 0·5 g. of iron in nitric acid and with excess of ammonia. The precipitate is collected, washed and dissolved in hydrochloric acid, and the precipitation with ammonia is repeated. From this point onward the general procedure is followed.

(5) *Tellurium in Lead and Galena.*—Twenty g. (or more) are dissolved in 150 ml. of hot 25 per cent. nitric acid. The lead is precipitated with excess of dilute sulphuric acid (1 : 1), and the lead sulphate is collected with the aid of slight suction and washed with 5 per cent. sulphuric acid. The filtrate is treated with 0·3 to 0·5 g. of iron in nitrate solution and then with ammonia, and the ferric hydroxide is collected, washed and treated as described.

When a gold ore is smelted with litharge and fluxes, any tellurium present passes into the lead button,[5] and may be determined therein by the method described above.

(6) *Oxidised Ores, etc.*—Oxidised material (iron ores, calcined blende, etc.), if attacked with hydrochloric acid, must be heated in a flask fitted with a reflux condenser; clayey or siliceous ores treated in this manner may cause trouble during the filtration of the insoluble matter, owing to colloidal silica, since the volatility of selenium precludes evaporation to dryness. If such ores are fused with sodium peroxide, the amount of material taken is limited by the capacity of the crucible, and gelatinous silica may still interfere in the subsequent operations. In such circumstances I have successfully applied decomposition by means of strong sulphuric acid. Twenty g. of ore are introduced into a 500-ml. Kjeldahl flask and

boiled with 50 ml. of strong sulphuric acid. The cooled acid is cautiously diluted with 50 to 75 ml. of water, 30 ml. of strong nitric acid are added, and the flask is again heated for some time. The contents are transferred to a beaker, diluted, and filtered from insoluble matter. The filtrate is treated with ammonia, ferric nitrate having been added if necessary.

The Kjeldahl digestion method is applied in the search for selenium in soils.[6]

(7) *Electrolytic Sludge.*—This material is often rich in selenium and tellurium, but nevertheless I have secured satisfactory results with cupriferous anode slimes containing 3 per cent. of selenium and 0·5 per cent. of tellurium by proceeding as follows:—One g. of material is digested with 25 ml. of strong nitric acid in a conical flask. The solution is diluted, filtered, and treated first with a solution of 1·2 g. of iron in nitric acid, and then with ammonia, and the precipitate is collected, dissolved, and re-precipitated. The subsequent treatment is the same as above, except that the precipitate produced by stannous chloride is digested with brominated acid in a flask instead of on the filter. In this way a more protracted attack is obtained, and less bromine is required. The hydrochloric acid solution is diluted with one-quarter of its volume of water and filtered through pulp, and the filtrate is treated with a slow current of sulphur dioxide.

(8) *Chamber mud* may be extracted with water and the residue digested with ammonium carbonate solution. The resultant lead carbonate, etc., is filtered off and treated with dilute nitric acid, the solution is decanted, and the residue is digested with stronger acid. The lead nitrate solution is treated with sulphuric acid (5, *supra*) and the lead sulphate is filtered off and rejected. All the extracts and filtrates are combined, acidified if necessary, and treated with ferric nitrate solution and ammonia, etc.

SUMMARY.—A process of fairly general applicability for the determination of subordinate amounts of selenium and tellurium is described. It consists in the following sequence of manipulations: acid attack, or fusion with sodium peroxide and solution in hydrochloric acid; precipitation of selenium and tellurium with ammonia on ferric hydroxide if copper and nitric acid have to be eliminated; precipitation of the two elements with stannous chloride; solution of the precipitate in brominated hydrochloric acid; precipitation of the solution with sulphur dioxide in two stages for the separation of selenium from tellurium. No evaporations of chloride solutions, and no precipitations with hydrogen sulphide or extractions with alkaline sulphide are involved. Directions are given for the application of the method to a variety of ores, metals and by-products.

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WASHINGTON SINGER LABORATORIES
UNIVERSITY COLLEGE, EXETER

February, 1939

A Method for the Determination of small Quantities of Boron in Plant Material

By KENNETH L. ROBINSON, B.Sc., B.Agr.

(*Read at the Meeting of the Scottish Section, February* 26, 1937)

The following method is one that has proved very satisfactory for the determination of small quantities of boron in connection with another investigation. Because of its high degree of sensitivity only relatively small amounts of plant material (generally about 1 g. of dry matter) are required, and this effects a saving both of time and of reagents.

When a solution of boric acid is brought into contact with turmeric a red colour is developed, slowly in the cold, more rapidly on heating; the intensity of the colour is increased by the presence of oxalic acid. Bertrand and Agulhon[1] estimated the boron content by the area of red colour produced on a strip of turmeric paper, under precisely defined conditions, but without heating. Cassal and Gerrans[2] allowed the colour to develop in tincture of turmeric evaporated on sand under the influence of heat, but this causes volatilisation of boric acid, which has to be trapped by a system of potash bulbs and re-estimated.

During the elaboration of the present method it was found that the volatilisation of boric acid, observed by Cassal and Gerrans, was largely due to the presence of ethyl alcohol, used as a solvent for the turmeric; presumably this leads to the formation of readily volatile ethyl borate. Accordingly, other means of preparing the turmeric reagent have been adopted, and these appear to give satisfactory results.

Certain substances hinder the development of the turmeric red colour (notably phosphates, silicates and salts of the alkali metals—sodium and potassium), and therefore have to be removed before this takes place. The most convenient means of effecting this is to treat the plant ash with phosphoric acid and methyl alcohol; the boron present can then be distilled off as methyl borate. This boron must be trapped in the distillate by the addition of a suitable hydroxide or carbonate, in order to form a non-volatile borate. The use of sodium hydroxide as the receiving alkali causes a diminution in the amount of colour developed by a given quantity of boron, but since this alkali was otherwise satisfactory, the extent of its colour hindrance was investigated, so that, if possible, modifications might be introduced which would permit of its being used.

It was found that, on using a constant amount of boron, addition of increasing amounts of sodium hydroxide produced an increasing depression of colour until a maximum depression was reached; further increases of soda had no further depressant action. Therefore, by employing a suitable and constant excess, sodium hydroxide could be used as the receiving alkali, for determinations within a given range of boron-contents.

Table I illustrates the effect of sodium hydroxide on varying amounts of boric acid, and Table II the effect of varying amounts of sodium hydroxide.

TABLE I

EFFECT OF SODIUM HYDROXIDE ON VARYING AMOUNTS OF BORIC ACID

	Lovibond red units	
B_2O_3 present mg.	No NaOH added	4 ml. of *N*/50 NaOH added
0·005	2·0	1·0
0·010	4·0	2·0
0·015	6·0	3·0
0·020	8·0	4·8
0·025	10·0	5·7
0·030	12·0	7·3

TABLE II

EFFECT OF VARYING AMOUNTS OF SODIUM HYDROXIDE

	Lovibond red units	
N/50 NaOH added ml.	0·020 mg. of B_2O_3 present	0·005 mg. of B_2O_3 present
0	8·0	2·0
2	5·9	1·0
4	4·8	1·0
6	4·0	1·0
8	4·0	1·0
10	4·0	1·0
12	4·0	1·0

It would appear that it is the ratio of sodium hydroxide to boron that affects the magnitude of colour formation, but that, provided that a certain ratio is exceeded, a uniform intensity of colour is developed from a constant quantity of boron.

DETAILS OF THE METHOD.—About 20 g. of turmeric powder are extracted with ether in a Soxhlet apparatus until the syphonings are colourless, and the yellow extract is then made up to 250 ml. with ether. Since contact with the air lessens the sensitivity of turmeric as a reagent for boron, different samples of powder may vary in effectiveness; thus the quantities of turmeric reagent prescribed in this paper may have to be increased, to ensure that an excess of reagent is present.

The ethereal extract is mixed with acid-washed silver sand in the proportions of 4 ml. of extract to 40 g. of sand. Thorough mixing, followed by evaporation on a water-bath, results in the sand grains being coated with turmeric and having the appearance of a yellow powder. This turmeric-coated sand is the final turmeric reagent, 40 g. (conveniently measured) being used for each determination.

To standardise the reagent, convenient amounts of standard boric acid solutions are evaporated to dryness—each with 0·5 ml. of *N* sodium hydroxide solution in porcelain basins. One ml. of water and 1 ml. of saturated oxalic acid solution are then added, and the residues in the basins are re-dissolved.

To the solutions, which should now be acid, 40 g. of turmeric reagent are added, and the mixtures are well stirred with a glass rod and heated to dryness on the water-bath. A further 1 ml. of oxalic acid solution is then added and, after again being thoroughly mixed, the contents of the basins are heated to dryness as before. The second addition of oxalic acid ensures that reaction between the turmeric and boron is complete.

The sand is next transferred to a Jena sintered-glass filter funnel (No. 11G1) and extracted with 70 per cent. alcohol until the filtrate is colourless. The extract is made up to 100 ml. and the intensity of red colour estimated by means of a Lovibond tintometer. Owing to the varying amounts of unchanged yellow turmeric present in this solution it is not possible to estimate the red colour satisfactorily with the ordinary type of colorimeter, and an instrument which can eliminate differences in tints is necessary. The colour is stable for 3 hours, even in sunlight, but then begins to fade slowly. If the coloured solutions are kept in the dark they remain unaltered for about a day.

Determinations of Boron in Plant Material.—A suitable quantity of plant material (about 1 g. of dry substance) is made alkaline with saturated barium hydroxide solution, in order to prevent subsequent loss of boron by volatilisation. The liquid is evaporated, the residue is ignited to a white ash, and the ash is transferred to a distillation flask; the dish is then washed with 5 ml. of orthophosphoric acid (sp.gr. 1·75), which is decanted into the distillation flask.

The type of distillation apparatus is indicated in Fig. 1.

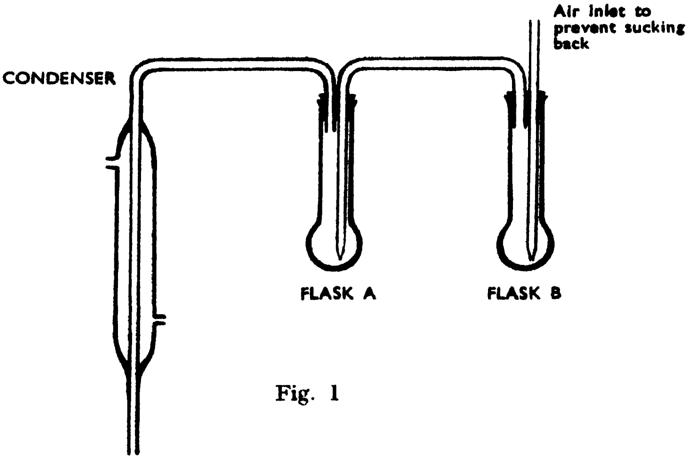

Fig. 1

Fifteen ml. of methyl alcohol (industrial 95 per cent.) are introduced into flask A, which contains the ash and phosphoric acid, and 25 ml. into flask B. Flask A is heated, by means of a boiling water-bath until all the alcohol has distilled over, the distillate being received in a flask containing 0·5 ml. of *N* sodium hydroxide solution; the end of the condenser must dip under the surface of this soda solution. Heat is next applied to flask B (the heating of flask A being meanwhile continued), with the result that a stream of alcohol vapour sweeps through flask A and volatilises the remaining boron; the complete distillation occupies about 30 minutes. The distillate is then evaporated to dryness, and the residue is treated in the same way as the standards.

Micro Kjeldahl digestion flasks are suitable for the distillation and can be sealed with rubber stoppers, but all glassware used must be free from boron, and the apparatus should be treated with cleansing solution (potassium dichromate and sulphuric acid). Industrial methyl alcohol may contain boron, which must be previously removed by distillation from sodium hydroxide; the receiver alkali is stored in a glass vessel free from boron. The turmeric reagent alone, when extracted with 70 per cent. alcohol, gives a red solution corresponding with about 1·0 Lovibond unit, and this value must therefore be deducted from all readings. Blank determinations are made when fresh supplies of turmeric reagent are prepared.

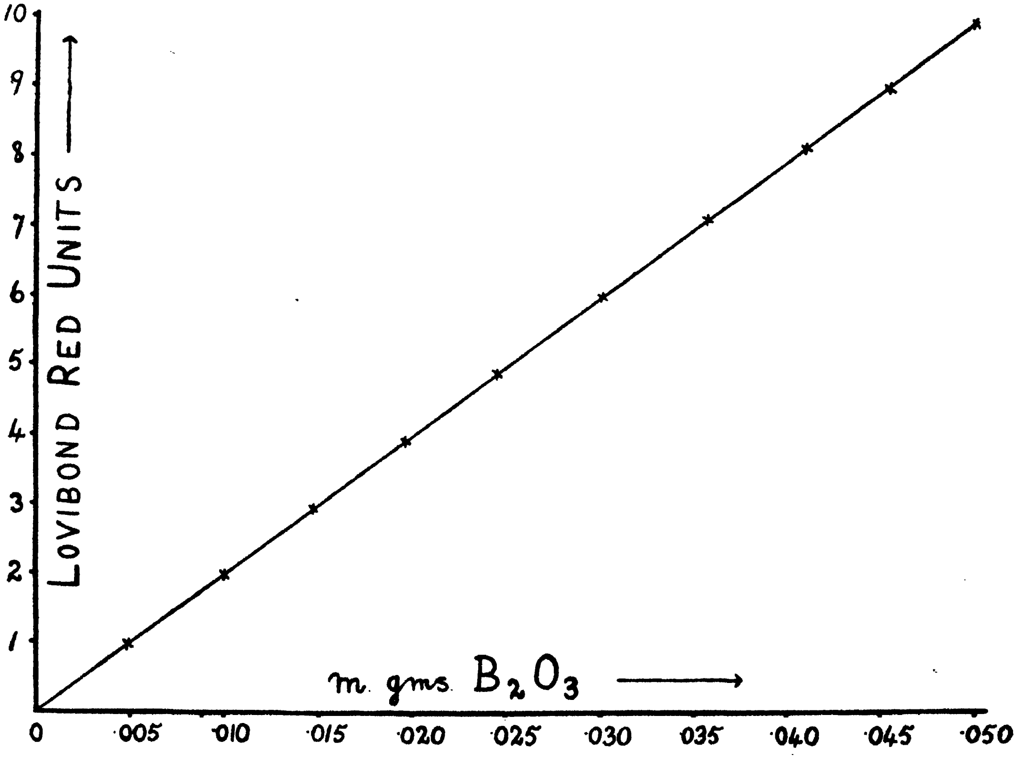

Fig. 2

Fig. 2 shows the graph for quantities of boron, as plotted against the corresponding Lovibond reading.

Table III gives figures illustrating the agreement between replicate determinations of boric acid standard solutions.

TABLE III

BORIC ACID STANDARDS

B_2O_3 mg.	Lovibond readings (red units)	B_2O_3 mg.	Lovibond readings (red units)	B_2O_3 mg.	Lovibond readings (red units)
0·005	1·0	0·015	2·7	0·04	8·0
	1·0		3·0		7·8
	0·9		3·0		8·0
	1·2		3·0		8·0
	1·0		2·8		8·1
	1·0		3·0		8·0
	1·0		3·0		8·2
	1·1		2·9		8·0
	0·9		2·9		8·1
	1·0		2·9		8·0
	1·0		3·0		7·9

Table IV gives figures illustrating the agreement between duplicate determinations on plant material.

TABLE IV

PLANT MATERIAL

Sample of dried substance (1 g.)	Lovibond reading (red units)	Sample of dried substance (1 g.)	Lovibond reading (red units)	Sample of dried substance (1 g.)	Lovibond reading (red units)
A	10·4	E	10·3	I	9·1
	10·4		10·3		9·3
B	9·7	F	9·6	J	14·0
	10·0		9·8		14·3
C	11·5	G	6·7	K	6·0
	11·5		6·5		6·0
D	12·7	H	7·5	L	4·4
	12·4		7·5		4·4

I wish to thank the Governors of the West of Scotland Agricultural College for the Colin Thomson Research Grant, which made this work possible; also, Professor D. N. McArthur and the staff of the Chemistry Department, the West of Scotland Agricultural College, for their guidance and never-failing interest and consideration.

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THE CHEMISTRY DEPARTMENT
THE WEST OF SCOTLAND AGRICULTURAL COLLEGE
GLASGOW, C.2

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Analysis of Vinegar

A Modified Method

BY E. T. ILLING, B.SC., F.I.C., AND E. G. WHITTLE, B.SC., A.I.C.

We should like to express our appreciation of the value of the method of Edwards and Nanji[1] for the analysis of vinegar. Their new tests are of great assistance in distinguishing between malt vinegar, vinegar other than malt vinegar, and artificial vinegar. When testing their methods, however, we found that some modification was desirable so as to reduce the amount of sample required and to save time. To confirm the results of all the determinations prior to issuing a certificate under the Food and Drugs (Adulteration) Act, it would be necessary to purchase about a quart of vinegar for division. The request for such a quantity would, in many instances, arouse suspicion and thus defeat the object of taking the sample. This difficulty has already been encountered. With a view to avoiding it, therefore, we have endeavoured to modify the method in such a way as to involve only one distillation, and yet to give results of the same order of magnitude as those obtained by Edwards and Nanji. With the oxidation and iodine values this was relatively easy, but the ester value presented many difficulties, and we have carried out a number of experiments with a solution of ethyl acetate and with malt vinegar and have introduced certain modifications to enable higher and more consistent results to be obtained.

Our results show that the greater the concentration of alcohol the more complete is the hydrolysis of ethyl acetate, but with vinegar distillates the reverse appears to hold good. Some of our results with malt vinegar suggested that the bulk of the esters were not obtained in the first 30 ml. of the distillate, and hence in the modified method we propose to take a portion of the whole distillate. Again, there appeared to be some loss of ester during the first stages of distillation, since, when a trap was employed, slightly higher values were obtained.

The modified method requires only 60 ml. of vinegar for the determination of the three values and only one distillation is necessary.

MODIFIED METHOD.—The method proposed is as follows:—The apparatus consists of a 350–ml. distilling flask, which is fitted with a rubber bung carrying a small separating funnel. The side-tube of the flask is bent so that it descends vertically into the opening of the condenser of double-surface pattern, and the lower opening of the condenser is fitted by means of a rubber stopper into one limb of a small U-tube, similar to a calcium chloride tube with bulbs, the other limb of which is fitted with a thistle safety-funnel with two bulbs.

Sixty ml. of vinegar are measured into the distillation flask and a little pumice is added. The cylinder used for measuring the vinegar is rinsed with 10 ml. of water, which is poured into the separating funnel, and 0·5 ml. of water is placed in the thistle funnel and 4·5 ml. in the U-tube to make a seal. The U-tube is marked on each limb at the level of 39·5 ml. The vinegar is distilled, and when about 20 ml. of distillate have been collected the thistle funnel is detached from the U-tube, and this tube is separated from the condenser and supported by any convenient means so that it is upright and the distillate drops into it. When the volume of the distillate has reached the marks the U-tube is removed and replaced by a 25-ml. cylinder. The distillation is continued until 10 ml. more have been collected, after which the 10 ml. of water are transferred from the separating funnel to the distilling flask, and the distillation is continued until a further 10 ml. have been collected, making 60 ml. in all, including the 5 ml. used as a trap. The distillates are transferred to a beaker and mixed, and the funnel and U-tube are rinsed with the mixed distillate. The procedure is then as follows:

(1) *Artificial vinegar or spirit vinegar.*—Ten ml. of the distillate are taken for the oxidation and iodine values, and the original method of Edwards and Nanji is followed.

TABLE I

MALT, CIDER AND ARTIFICIAL VINEGAR

Sample	Oxidation value			Iodine value			Ester value			Remarks
	Original method	Modified, without trap	Modified	Original method	Modified, without trap	Modified	Original method	Modified, without trap	Modified	
Malt vinegar A	876	1160*	—	804	780*	—	23	60*	—	* 60 ml.; distilled 18 ml.; added 15 ml. of water, distillation continued to give 60 ml.
,, ,, B	840	870*	—	954	950*	—	33	70*	—	
,, ,, C	904	1040	1010	960	960	950	24	60	100	
,, ,, D	1410	(*a*)1030 (*b*)1180	(*a*)1210 (*b*)1070	1004	(*a*)1050 (*b*)1050	(*a*)1050 (*b*)1040	33	(*a*)115 (*b*)125	(*a*)115 (*b*)135	Series (*b*) repeated some days after the first series (*a*)
,, ,, E	600	660	650	840	860	860	27	110	130	
,, ,, F	—	—	750	—	—	1260	—	—	120	
,, ,, G	—	—	740	—	—	1250	—	—	135	
,, ,, H	—	—	750	—	—	1000	—	—	135	
Artificial vinegar I	14	12	—	11	11	—	nil*	4	—	* slight negative value
,, ,, J	10	10	—	12	12	—	nil	nil	—	
,, ,, K	9	9	17	4	7	14	1	6	nil	
,, ,, L	—	4	4	—	18	17	—	nil	nil	
Source unknown M	440	450	480	550	555	540	23	70	100	
Cider vinegar N	204	266	260	328	336	342	14	70	79	

(2) *Malt vinegar, or distilled malt vinegar.*—Five ml. of the distillate are taken for the oxidation and iodine values and the original method is followed except that for the oxidation value 15 ml. of $N/10$ potassium permanganate solution are used.

For (1) values are given by 20 (A–B); for (2) by 40 (A–B).*

Ester value.—Twenty-five ml. of the distillate are taken, 0·5 ml. of phenolphthalein solution are added, and the original method is followed. After the heating under reflux is finished, 1·0 ml. of phenolphthalein solution is added, and with malt vinegar (in which the reddish-brown colour of the hydrolysed liquid obscures the end-point when undiluted) 100 ml. of distilled water are added, and the excess of alkali is titrated with $N/50$ hydrochloric acid.

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* A represents the number of ml. required in the blank test, B that required in the actual test.

Ester value = 8 (A–B)*

The modified method without the trap is very simple. Sixty ml. of vinegar are distilled and 15 ml. of water are placed in the separating funnel. When 45 ml. of distillate have been collected the water in the separating funnel is run into the distillation flask, and the distillation is continued until 60 ml. (in all) have been collected.

A few analyses comparing the different methods are given in Tables I and II.

TABLE II

SPIRIT VINEGARS

Sample	Period of storage Months	Acetic acid Per cent. w/v	Oxidation value Original method	Oxidation value Modified	Iodine value Original method	Iodine value Modified	Ester value Original method	Ester value Modified
A.	12	4·36	103	101	13	16	nil	nil
B.	12	4·20	186	204	5	6	6	11
C.	6	4·34	29	26	6	6	nil	nil
D.	6	4·20	94	100	5	4	5	3
E.	1	4·37	220	270	13	20	7	14
F.	1	4·21	206	234	6	4	10	14

Samples B, D and F were prepared in the laboratory by dilution of vinegars of 12 per cent. strength to 4 per cent. All these samples had been matured for 6 months in addition to the period of storage.

These results for spirit vinegars confirm the findings of Edwards and Nanji, that the storage of these vinegars of 4 per cent. strength affects the oxidation value to a pronounced extent. This effect is apparently very variable, as vinegar B, when diluted and stored for 12 months, lost 50 per cent. of its oxidisable compounds (*cf.* vinegar A), whereas vinegar D, when diluted and stored for 6 months, lost 74 per cent. of these compounds (*cf.* vinegar C). This variation lends support to the suggestion that the change is due to uncontrolled biological, rather than to chemical, action.

The analysis of sample M (Table I) shows the desirability of being able to obtain the three values from one distillation. The sample was bought as vinegar, and the purchase price was only 2½d. per pint; the vendor refused to sell it as malt vinegar. The original method of Edwards and Nanji was carried out, and for both the oxidation and iodine values the amounts of the reagents added were found to be insufficient, owing to the fact that the sample was malt vinegar, or more probably a mixture. Another distillation had to be made to obtain the values given above. By using the modified method the whole work was completed on the distillate of 60 ml. of vinegar, with a great saving of sample, time and labour.

Our thanks are due to Mr. D. R. Wood for his very helpful criticism, and to British Vinegars, Limited, for kindly supplying samples of spirit vinegar, with information about their storage.

REFERENCE

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THE SOMERSET COUNTY LABORATORY
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February, 1939

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* A represents the number of ml. required in the blank test, B that required in the actual test.

The Analysis and Differentiation of the Composition of Iron, Phosphorus and Calcium Compounds in respect of Nutritional Requirements

THE following papers were read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry on February 1st, 1939.

I. INTRODUCTION

BY J. C. DRUMMOND, D.SC., F.I.C.

It is nearly a century ago that the first estimates of man's food requirements based on chemical analyses were put forward. Liebig was the pioneer. He elaborated Magendie's ideas on the part played by the "carbonaceous and azotised foods" into a working scheme in which a measure of the heat-producing "respiratory elements of nutrition" was derived from the carbon-content of the food, while for quantitative estimates of blood and tissue-forming "plastic elements" reliance was placed on analyses for nitrogen.

Not long before Lyon Playfair brought Liebig's early quantitative studies to the notice of English science *The Lancet* had drawn attention to the lack of knowledge regarding the nature of the food requirements of man. It called for the application of the "elements of weight, and time, and number" to these problems, so that a new branch of science, which the versatile Count Rumford had already called "The Science of Nutrition," could be opened up.

Liebig's work gave considerable impetus to the analytical study of foods. Much of the early work reflects the current views that estimates of carbon and nitrogen provided a measure of the nutritive value of a foodstuff. Many people took up the challenge implicit in the remark of Sharpey, the father of English physiology: "We are sorely in want of trustworthy data to show the absolute quantities of carbon and nitrogen indispensable for health under different circumstances." Lyon Playfair was one. Some of his estimates of the food value of diets are given below, with the object of bringing home to you that we are very much in the same position to-day in respect of our ideas on the requirements for the three elements we are to consider to-night as Lyon Playfair, Letheby, Edward Smith and other pioneers were with regard to the problem of deciding how much nitrogen and carbon a diet should contain.

Diet	Weight per week oz.	Nitrogenous ingredients oz.	Non-nitrogenous ingredients oz.	Carbon oz.	Ratio of heat-givers to flesh-formers
English soldier ..	378	36·15	127·18	71·68	3·66
,, sailor ..	302	34·82	102·89	70·55	3·70
Christ's Hospital ..	216	17·16	61·27	39·18	4·21
English prisons (Class 2, males) ..	206·5	15·28	111·85	59·23	7·13

They had to do the best they could with such information as that bread contains 125 grains of carbon and 5·5 grains of nitrogen per ounce. Until very recently we had very little more to help us in forming our estimates of mineral requirements than bare analytical records, such as that "peaches, stones discarded, skin included" contain 9·1 mg. of Ca, 4·8 mg. of P and 18·5 mg. of Fe per 100 g. Laboratory researches of the past few years have revealed, however, the limited value of such information and have shown that it is a much more vital matter to know something about the availability of these elements to the organism and about factors that may influence their absorption or utilisation. The question has already grown to be one of more than academic interest; it has become one of vital national importance. The dietary surveys of E. M. H. Lloyd, Sir John Orr, Sir William Crawford, H. Broadley, and many others, leave not the slightest doubt that a proportion of our population, certainly not less than half, and possibly a good deal higher, for it may well be that our standards are too low, exists in a state of chronic starvation in respect of calcium, phosphorus, iron and most of the essential vitamins. With the latter we are not concerned to-night, nor can we spare time to discuss whether the indications of the trend of British agriculture towards increased production of grass, milk and garden produce are strong enough to encourage the hope that we shall achieve in this country the "marriage" between agriculture and public health about which so much has been said. What concerns us to-night is the progress that has recently been made, and that which is likely to be made in the near future, in studying the nature of the compounds of iron, calcium and phosphorus which are found in foods, and their fate in the animal body.

It is no longer possible to accept without reservation the bare statement that the daily requirements of an adult for these elements are 1·0 g. of calcium, 1·5 g. of phosphorus and 15 mg. of iron. Taken by and large, a mixed diet providing these amounts would probably be adequate, but it is not difficult to imagine a diet compounded on the basis of the figures in analytical tables which might comply with these requirements but which, in actual fact, would be defective. Red meat is often popularly regarded as body-building because it contains plenty of iron (about 8 mg. per 100 g.). Half-a-pound of steak might, therefore, be regarded as sufficient to cover the daily requirements of iron. Actually, the availability of the iron compounds in cooked muscle tissue is of a very low order, only about 10 to 20 per cent. being absorbed into the blood stream. The half-pound of steak would, therefore, provide a mere 2 or 3 mg. of iron.

It is facts such as these that have to be kept in mind, not so much when we are considering the meals of the relatively well-to-do, as when we look at the family budgets of the poor and find that the foods their limited means enable them to purchase seldom provide more than 8 or 9 mg. of iron in all forms. On this subject Dr. McCance will be giving us the benefit of the wide experience he has gained in studying the availability of the iron compounds in foods.

I had been hoping that it might be possible for Professor Kay and Professor Dodds to address you side by side as a pair of nutritionally-minded Siamese twins, so inextricably is the study of the phosphorus compounds of foods linked with that of the compounds of calcium. I have only to remind you how large a proportion of phosphorus in certain vegetable foods may be represented by phytin, and how such phosphorus may not only escape utilisation itself, but may also make matters worse by inhibiting the absorption of calcium. Modern studies of the calcification of bone and teeth are being influenced to-day more by considerations of the significance of calcium and phosphorus intakes and the ratio of calcium to phosphorus than by views on the part played by vitamin D. The pendulum is swinging quite a long way back. I think it will soon be realised that we have tended to over-emphasise the importance of the antirachitic vitamins. Most of us are living on subnormal intakes of calcium and on diets showing lower ratios of calcium to phosphorus than is desirable (below 0·5). Probably for this reason we often need unnaturally high dosages of materials providing vitamin D_2 or D_3 in order that these agents, in their mysterious way, shall improve a defective absorption of bone-forming elements. They help us to make the best of a bad state of affairs. We are fortunate in being able to turn to halibut-liver oil or calciferol to get such high doses of D vitamins, for it would go hard with us if we had to rely on the common natural foods which, with the exception of eggs and "summer" butter, are so curiously deficient in vitamins of the D group. The indications are that Nature intended us to grow strong bones and good firm teeth without dependence on the extraordinary reserves stored in the livers of strange fish. In the days when the diet of the hard-working peasant of England was largely composed of coarse wholemeal wheat and rye bread and the "white meats"—milk, whey, cheese and eggs,—rickets seems to have been almost unknown. Such diets provided as much as 1·5 to 2 g. of calcium and rather more phosphorus. Because these intakes were so high and the ratio of calcium to phosphorus was satisfactory (about 1) very little vitamin D was needed. In actual fact the daily intake of vitamin D could seldom have been more than 50 international units, and may often have been much lower. Such intakes, when found to-day, are usually associated with low calcium diets and rickets. That is why we have in mind doses of 100 to 250 units for adults and 250 to 1000 units for children.

We have recently examined in my laboratory the vitamin D content of a considerable number of human milks—it is curious that this has not been done before—and we find the mean value to be 3·5 units per 100 ml. That means that a suckling infant gets in its early life from about 15 units daily, and about 35 units daily at weaning. It is rare to find a rachitic state developing in a breast-fed infant unless the supply of milk fails. Such relatively small amounts of vitamin D are presumably ample, therefore, to enable the growing infant to assimilate perfectly the bone-forming minerals of its natural food. Contrast the conditions when an infant is being artificially reared on cows' milk. In spite of providing, weight for weight, approximately four times the amount of calcium and six times the amount of phosphorus found in human milk, this food may need supplementing with an antirachitic preparation supplying from 100 to 500 units daily before one can be certain of full protection against rickets.

Such are the problems that make us look with suspicion on columns of figures giving the percentage of calcium, phosphorus and iron in foodstuffs. What hope we have of obtaining more precise information, and what likelihood there is of our being able to draw up columns of figures which will be as much in advance of our present tables as our modern reference data about the nutritive value of proteins are ahead of the old estimates of nitrogen of a century ago, are matters on which the following contributions, dealing with the progress made in various directions, should enable us to form an opinion.

II. THE IONISABLE AND AVAILABLE IRON IN FOODS*

By R. A. McCance, M.A., Ph.D., M.D.

(*Abstract*)

STUDENTS of nutrition now consider that iron is more likely to be utilised if taken in inorganic than organic form, although they are agreed that even in the inorganic form it is not freely absorbed as is, for example, sodium. Ferrous salts are probably absorbed more easily than ferric salts, but, if the intake is large enough, *small* quantities of either ion reach the general circulation. This may also be assumed for the inorganic iron in food.

In 1930, Hill (*Proc. Roy. Soc.*, 1930, B., **107**, 205) introduced a method of determining small quantities of ferrous iron based upon its reaction with $\alpha\alpha'$-dipyridyl (Blau, *Monatsh. Chem.*, 1898, **19**, 647). By the use of a suitable reducing agent both ferric and ferrous ions were made to react, whilst haematin iron was shown not to do so. Elvehjem *et al.* (*J. Biol. Chem.*, 1933, **103**, 61) and Sherman, Elvehjem and Hart (*J. Biol. Chem.*, 1934, **107**, 383; Abst., ANALYST, 1934, **59**, 49) found that chemical determinations of ionisable iron agreed well with biological determinations of "available" iron. Other investigators have followed the same method, but the results have shown pronounced discrepancies, probably due to one or more of the following causes:—(i) The samples analysed by different chemists were not the same, or even grown in the same part of the world. (ii) The results are expressed, not as absolute amounts of ionisable iron, but as the percentage of the total ionisable iron. The figures therefore depend upon the ratio of two colorimetric determinations—one of total and the other of ionisable iron. On the other hand, Shackleton and McCance's results (*Biochem. J.*, 1936, **30**, 582; Abst., ANALYST, 1936, **61**, 490) suggested that in any one material the percentage of total iron found to react with $\alpha\alpha'$-dipyridyl tended to be a much more constant figure than the absolute amount of reactive iron, so that, if the technical difficulties could be overcome, expressing the reactive iron as a percentage of the total iron should lead to more consistent results than giving it as absolute amounts of the metal. (iii) The determination of ionisable iron by any method is beset with difficulties. The two chief troubles with the dipyridyl method are (*a*) the contamination of the dipyridyl red with yellow pigments; Shackleton and McCance (*loc. cit.*) avoided the difficulty by the use of a comparator; (*b*) adsorption of the coloured complex on to matter which is filtered off before the colour comparison is made. The original Wisconsin method (and probably also the later modifications) was liable to this error. (iv) The procedure may alter the amount of the "organic" iron that can be made to react with dipyridyl. Haematin iron does not react, whatever method is followed, but, according to Hill (unpublished communication), such compounds account for only a small fraction of the iron in foods that is resistant to the reagent. The remainder may react slowly or to a different extent if the conditions are modified.

The biological assessment of available iron has, in the main, been carried out with rats, but a few attempts have been made with human subjects. A dog technique was introduced in 1935, but the results do not appear to have been compared with those obtained with dipyridyl. The published results of different workers indicate that general agreement between the figures obtained by the rat

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* To be published in *Chemistry and Industry*.

and the dog methods should not be expected. Comparisons that have been made between ionisable iron (by chemical methods) and available iron (by rat assay) suggest that there is some basis for the Wisconsin view that the chemical method affords an indication of the available iron as determined by the young rat method. If, however, only a small percentage of the iron resistant to dipyridyl is haematin iron, there is no theoretical reason why the results should agree. Recent work (Fischer and Hultzsch, *Biochem. Z.*, 1938, **299**, 104) suggests that the non-haematin iron which does not react with dipyridyl may be in combination with organic phosphorus. A further problem awaiting solution is whether in all or any tissues the ionisable iron bears a constant relationship to the total iron or whether each varies independently of the other. The value of chemical and biological assays would be greatly enhanced if it could be shown that the results were applicable to man. Superficially it appears that the problem might be investigated by balance experiments (Schultz *et al.*, *J. Paediat.*, 1937, **10**, 147), but practical limits of dosage may be a serious difficulty (Stearns and Stinger, *J. Nutrition*, 1937, **13**, 127). In all probability if the ionisable iron in food should prove to be equal to the available iron as determined by animal experiment, it may be assumed that the results apply to man, but it will be exceedingly difficult to prove or disprove it.

III. PHOSPHORUS COMPOUNDS IN RELATION TO NUTRITION

By H. D. Kay, O.B.E., D.Sc.

(Abstract)

IN certain respects the nutritive values of phosphorus and calcium are interdependent. In man, about 90 per cent. of the total phosphorus present is in the bones, about 8 per cent. in the muscles, and smaller quantities in the brain and the blood. The human adult requires about 1 g. of phosphorus per day, whilst the growing child requires on the average rather more. The types of phosphorus compounds ingested include (*a*) inorganic phosphate, (*b*) phosphoric esters, (*c*) phosphagen (unlikely to be much), (*d*) phospholipins, (*e*) nucleic acids, (*f*) phosphoprotein. It is probable that all phosphorus esters are hydrolysed prior to absorption from the gut. There is little, if any, phosphatase in the stomach, but plenty in the intestinal juice and mucosa.

AVAILABILITY OF PHOSPHORUS OF THE FOOD FOR NUTRITIONAL PURPOSES.—In the growing animal a diet rich in calcium but poor in phosphorus produces rickets; if inorganic phosphorus is added, the diet ceases to be rachitogenic in rats and becomes less so in puppies. The total phosphorus in a given diet does not necessarily indicate the amount of phosphorus available for the nutrition of the animal ingesting it. At least one substance, phytin (inositol hexaphosphoric ester) is not in fact hydrolysed completely in passing through the intestinal tract, and can be found in the faeces of dogs, rats or human beings who have eaten food containing it. The rachitogenic effect of certain diets containing large quantities of oatmeal or maize meal is due, at least in large part and perhaps completely, to the fact that most of the phosphorus in these grains is present as phytin. In an average middle class human diet, however, less than 5 per cent. of the total phosphorus is present as phytin phosphorus. Calcium carbonate inhibits the hydrolysis of phytin in the rat's gut, but phytin given to rats fed on a low calcium and phosphorus diet may be substantially hydrolysed, probably owing to the presence of phytase in the intestinal flora. The extensive fermentation which takes place in the alimentary tract of the ruminant probably ensures that phytin phosphorus is nutritionally completely available for this type of animal.

BERYLLIUM RICKETS.—The presence of calcium or other metals forming insoluble or difficultly-soluble phosphorus compounds seriously interferes with the apparent phosphorus value of a diet. This is strikingly shown in recent experiments on the phenomenon of beryllium rickets. If to the normal stock diet of growing rats 0·5 to 1·0 per cent. of beryllium carbonate is added, severe rickets is readily produced. This is due to the practical insolubility of beryllium phosphate even at *p*H 4·0. Even with normal diets rich in vitamin D, the precipitation of beryllium phosphate in the intestine makes the phosphate shortage in the body very acute. Moreover, the urinary excretion of phosphorus practically ceases, all of it being diverted to the faeces. Very little phosphate and calcium is retained in the animals taking beryllium carbonate, and far more calcium is excreted in the urine than in that of normal animals.

It is well known that a large excess of calcium in the diet interferes with the absorption of phosphorus; this is probably due to the precipitation of phosphorus in an insoluble non-absorbable form. Excess of iron, manganese or aluminium is said to have a similar effect.

USE OF RADIOACTIVE PHOSPHORUS AS AN INDICATOR.—A recent promising method of studying phosphorus metabolism and absorption depends upon the use of radioactive phosphorus (atomic weight 32) as an indicator. Radioactive P_{32} has a conveniently long life (half-life = 14·8 days), and is indistinguishable in chemical behaviour from P_{31}. It is prepared by the action of neutrons from radium mixed with beryllium on the sulphur of carbon disulphide, or by bombarding red phosphorus with deuterium ions of high energy. After treatment with nitric acid it can be converted into phosphate, which can be used for feeding and other purposes. A very small Geiger counter with a thin aluminium or mica window is used for determining the radioactivity of various compounds after this active phosphorus has been fed to animals. The method is very sensitive, and from 10^{-10} to 10^{-11} g. of radioactive phosphorus can thus be traced in an animal's tissues. The use of the cyclotron for the bombardment of red phosphorus enables preparations with great P_{32} activity to be obtained; a Lauritzen electroscope, which is more easily handled, may then be used for the radioactivity determinations. Results have been published by Hevesy (Denmark) and by a number of American workers.

FATE OF INGESTED PHOSPHORUS.—Results obtained by this method have shown that ingested inorganic phosphorus is largely taken up by the bones, whilst the greater part of the remainder is found in the muscles, digestive tract and liver. About a third of the total phosphorus ingested by human subjects is excreted in the faeces. Slow faecal excretion of phosphorus, re-excreted into the alimentary tract, continues for weeks. It has been calculated that about 1/400 part of the bone phosphorus is changed every hour and that about 1/20 of the muscle inorganic phosphorus is renewed in one hour.

Phosphorus atoms in an organic molecule, *e.g.* lecithin, caseinogen, do not exchange places with radioactive inorganic or organic phosphorus *in vitro*, but will do so in presence of enzymes. The organic phosphorus compounds that appear soonest in the tissues after ingestion of inorganic phosphate are creatine phosphate (of muscle) and adenosine triphosphate and hexose-phosphate. The ester phosphorus (presumably diphosphoglyceric acid) of red cells is rapidly formed.

The method has shown that in the laying hen practically no egg phosphatides are formed in the ovary, but that they are taken from the circulating blood-plasma by the ovary and incorporated in the yolk. The liver forms the phosphatides, which are then transported by the blood to the ovary. Apparently no phosphatides are formed in the red cells.

It has been found that the inorganic phosphorus of the blood and not the phospholipin phosphorus is the source of the various phosphorus compounds of milk; this confirms work done at Shinfield. From 1½ to 2 hours are required for the inorganic phosphorus actually in the mammary gland to be replaced by the circulating phosphorus. Casein phosphorus is formed rather more slowly than milk inorganic phosphorus; *i.e.* the latter must first diffuse into the gland, and the synthesis then takes some time. Milk phosphatide appears to be formed from inorganic phosphorus in the mammary gland. Ester phosphorus in milk is formed rather more slowly than casein phosphorus, but, like casein phosphorus, is also formed from circulating inorganic phosphorus.

IV. CALCIUM COMPOUNDS IN RELATION TO NUTRITION

By E. C. Dodds, M.V.O., D.Sc., M.D., B.S., F.R.C.P., and
J. D. Robertson, D.Sc., M.D., Ph.D., Ch.B., D.P.H.

(*Abstract*)

It has been established that there is a relationship between the parathyroid glands and calcium metabolism—between hyperparathyroidism or hyperfunction and increased calcium excretion leading to decalcification of the bones, and between hypoparathyroidism or underfunction and tetany. The level of serum calcium alone, however, gives no indication of the direction of the flow of calcium—whether into the bones or to the excretory channels. In assessing the calcium metabolism either in disease or following the administration of calcium compounds, it is necessary to note accurately the total calcium intake and output. For determining a calcium balance the following points are of importance:

(1) All food must be cooked with distilled water, and all dishes and saucepans used must be washed in distilled water. A duplicate diet is also sent to the laboratory for analysis. Only distilled water is given to drink.
(2) Urine is collected in Winchester bottles and sent to the laboratory each morning. Stools are received in special bowls fitted with lids. All receptacles are kept in refrigerators by the bedside.
(3) Two capsules, each containing 0·6 g. of carmine, are given after three days of the diet, and again at three daily intervals, until the required number of specimens have been obtained. The first carmine stool received, after the administration of carmine, belongs to the preceding period. Cascara evacuant in distilled water is the only aperient used.

In the experiments described the standard diet was so prepared that the calcium-content varied from 100 to 130 mg. daily, the acid and base being balanced. The daily calorific value of the food was varied to suit individual requirements by adding foodstuffs very low in calcium-content.

Variations in the proportions of calcium in foodstuffs made the analysis of a duplicate diet essential. For example, the published value for the calcium-content of marmalade is 0·012 per cent., whilst the value found was 0·071 per cent.

A comparison of the calculated values (for a three-days' diet) of the low calcium diets with the values found gave the following results: Calculated, 0·3 to 0·4 g.; found, 0·18 to 0·35 g.

Analysis of Mixed Diet or Faeces.—To facilitate fine sub-division of the dried material, the fat and a large proportion of the water were first removed by treatment with acetone. The process, as applied to faeces, was as follows:—Each specimen was thoroughly mixed with twice its volume of acetone, and after an hour all the specimens of the three-day period were filtered in a large Buchner funnel with the aid of suction. The filtrate was measured and either mixed with the three days' supply of urine or analysed separately. The residue on the filter-paper was warmed to expel the excess of acetone, dried, and ground to a fine powder in a mechanical grinder. By keeping the butter-fat separate from the rest of the diet it was usually possible to make the analysis without acetone extraction.

The diet was minced, dried at 105° C., weighed and ground to a fine powder mechanically.

Samples containing 6 to 20 mg. of calcium were taken for the analysis. For the diet, 30 g. of the powdered sample and its equivalent of butter-fat were weighed into the same dish. For urine, usually 100 ml. were evaporated in a porcelain dish. The sample of faeces, usually 1 g., was weighed into a dish containing the equivalent of the acetone extract of the faeces, which had been evaporated to dryness. The dishes were placed overnight in a muffle-furnace at 500° C., and on the following day the ash was dissolved in hydrochloric acid, the calcium was precipitated as oxalate, the precipitate was washed and dissolved in N sulphuric acid, and the solution was titrated with $N/10$ potassium permanganate solution in the usual way.

CALCIUM REQUIREMENTS.—The daily requirement of an adult is believed to be between 0·4 and 1·0 g. daily. On a low calcium intake of 0·3 g. in a three-day period there is a negative balance or calcium loss of 0·4 to 0·5 g. In pregnancy the subject excretes the same amount of calcium despite the supply of calcium to the foetus. The factors that influence the absorption of calcium salts are summarised as follows:

(i) *Composition of the diet.*—The ratio of calcium to phosphorus should normally be 2 : 1. If phosphorus is greatly in excess of this ratio, the calcium will be precipitated in the gut as tertiary calcium phosphate. This also happens if the calcium is greatly in excess.
(ii) The presence of free hydrochloric acid in the stomach promotes the absorption of calcium.
(iii) Lactose is believed to promote absorption if given with calcium.
(iv) Failure of fat absorption in subjects results in deficient calcium absorption.
(v) Vitamin D influences the absorption of calcium and phosphorus from the intestinal tract.

Third Report of the Sub-Committee on the Determination of Arsenic, Lead and other Poisonous Metals in Food-colouring Materials to the Analytical Methods Committee of the Society of Public Analysts

III. THE DETERMINATION OF COPPER

THE Sub-Committee was convened by the Committee and consisted of the following members:

T. Macara, F.I.C. (Chairman), nominated by the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades.
S. G. Clifford, A.I.C. (Hon. Sec.), nominated by the Oil and Colour Chemists' Association.
W. G. Messenger, B.Sc., F.I.C., nominated by the Society of Public Analysts and other Analytical Chemists.
J. R. Nicholls, B.Sc., F.I.C., nominated by the Government Chemist.
N. Strafford, M.Sc., F.I.C., nominated by Imperial Chemical Industries, Ltd. (Dyestuffs Group).
F. Thomas, M.Sc., nominated by the Society of Public Analysts and other Analytical Chemists.
H. Drake-Law, D.Sc., F.I.C., nominated by the Society of Public Analysts and other Analytical Chemists.

The present Report deals with the determination of copper in food-colouring materials, and recommends a method, which is described in the Appendix (p. 342).

PRELIMINARY TREATMENT OF THE FOOD-COLOURING MATERIAL.—Before copper can be determined in food-colouring materials it is necessary to destroy organic matter. Two general processes are available for this purpose, *viz.* ashing and wet oxidation. While ashing is usually the simpler process there can be no general certainty that the whole of the metallic impurities will be retained, since it is possible that copper may be lost during burning. In addition, very finely divided material may be lost unavoidably during fuming and, moreover, certain dyestuffs decompose with considerable violence. The Sub-Committee considered that a wet oxidation as described in the Report on the Determination of Arsenic (ANALYST, 1930, **55**, 102) was desirable. Such preliminary treatment was also prescribed in the Report on the Determination of Lead (ANALYST, 1935, **60**, 541), and since the examination of a colour for metallic impurities involves *inter alia* determination of both lead and copper, it would be advantageous to employ a method whereby both copper and lead could be determined on the same portion of the sample.

SEPARATION OF THE COPPER.—The method described in the previous Report for the Determination of Lead (*loc. cit.*) involves a wet oxidation of the sample, a sulphide precipitation under controlled conditions of acidity, and the re-precipitation of the lead as sulphate. It has been shown that copper is quantitatively precipitated with the lead sulphide and that the acid-alcohol-water filtrate from the lead sulphate contains the whole of the copper. This filtrate, which may contain traces of other metals, is suitable for the determination of copper.

COLORIMETRIC DETERMINATION OF COPPER.—Several reagents have been proposed in this connection and, in the opinion of the Sub-Committee, one of the best is sodium diethyldithiocarbamate, $(C_2H_5)_2N.CSSNa$, described by Callan and Henderson (ANALYST, 1929, **54**, 650). The reaction is delicate and the colour produced in acid or ammoniacal solution—golden brown at appropriate dilution—is suitable for colorimetric work. The addition of a little gum arabic gives a bright solution stable for several hours.

In sufficient concentration most of the common heavy metals give colours or turbidities with this reagent. Some of these metals, if present, would be found in the filtrate from the lead sulphate determination. The Sub-Committee is of the opinion that in dealing with the particular case of food-colouring materials it is unnecessary to provide for the case where relatively large proportions (several hundreds of parts per million) of unusual impurities (*e.g.* antimony, bismuth, cadmium, mercury, silver) are present. The proportions of such metals which are likely to be present in food-colouring materials have been shown to be without effect upon the determination of copper as described in this Report.

Residual iron and/or aluminium in the filtrate from the lead sulphate determination can be removed by treatment of the solution with ammonia, boiling and filtering, the precipitate being then dissolved in acid and re-precipitated with ammonia to avoid slight losses of copper. The precipitate carries with it traces of other metals, and the combined ammoniacal filtrates can be used directly for the determination of copper.

In the majority of cases the precipitation with ammonia can be omitted, the effect of interfering metals being suppressed by the addition of sufficient ammonium citrate before adding ammonia. When the ammoniacal citrate solution is coloured or is turbid, precipitation with ammonia (without the addition of citrate) must be employed.

The coloured complex produced by copper with diethyldithiocarbamate is soluble in some organic liquids and can be completely extracted with a suitable solvent, such as chloroform. In certain circumstances such an extraction of the colour, with subsequent colorimetric determination in the organic solvent, may be a desirable procedure to follow, *e.g.* when a turbidity is produced on the addition of sodium diethyldithiocarbamate due to an unusual impurity. The Sub-Committee after investigation is of the opinion that the method appended (page 342) is preferable.

ACCURACY OF THE COLORIMETRIC COMPARISONS.—It was considered desirable to investigate the accuracy with which the copper diethyldithiocarbamate colour can be matched by different individuals.

Several solutions containing different amounts of copper were compared in 100-ml. Nessler tubes with a series of standards, the observers estimating the amounts of copper, which were of course unknown to them. Comparisons were made by three to five observers in each of five laboratories, and the results are summarised in the following table; in only one instance was the extreme error greater than 4 per cent.

Approximate amount of copper solution in ml. (1 ml. = 0·00001 g. of Cu in 100 ml.)	Extreme error, as percentage of the amount of Cu present	Mean error as percentage of the amount of Cu present
4	± 2½	1½
6	−6	2
8	+4	1¼
10	−2	1

ACCURACY OF THE COMPLETE PROCESS.—An acid solution was circulated containing a known amount of copper sulphate together with salts containing iron, aluminium, lead, tin, zinc, calcium and phosphates.* This solution was assumed to be the product of the wet oxidation of a colouring material and the copper was determined by submitting the solution to the complete process starting from this stage.

The results obtained expressed as parts of copper per million in the hypothetical dyestuff were:

Actual copper present		24·2
Copper found by observer	(A)	26·4
,, ,, ,, ,,	(B)	25·8
,, ,, ,, ,,	(C)	22·7
,, ,, ,, ,,	(D)	23·8
,, ,, ,, ,,	(E)	24·9
,, ,, ,, ,,	(F)	25·5
Mean		24·85
Extreme variations from true copper content		−1·5 +2·2
Maximum deviation expressed as per cent. of mean		−6·2 +9·1

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* Equivalent to a hypothetical dyestuff containing:

Copper	24·2	parts per million
Iron, approx.	400	,, ,, ,,
Aluminium, approx.	400	,, ,, ,,
Phosphates (P_2O_5), approx.	200	,, ,, ,,
Calcium	40	,, ,, ,,
Zinc	35	,, ,, ,,
Tin	35	,, ,, ,,
Lead	10	,, ,, ,,

The actual figure obtained represents the difference between the copper found in the test solution and that found in the blank test on the reagents. Both of these determinations are subject to the errors of visual comparison. (See Lead Report, ANALYST, 1935, **60**, 548.)

EXAMINATION OF DYESTUFFS.—Seven dyestuffs were circulated for application of the complete process as described below. The results were:

	Parts Cu per million of dyestuff Observer					
Dyestuff	A	B	C	D	E	F
Ponceau	5	3½	4	4½	4½	4½
Nigrosine	12	14	14½	11½	13	12
Magenta	31½	32	32	28½	34½	29½
Geranine	32½	36	34½	32	32	33½
Iron oxide	101	—	96	107	104	104
Carmine	36	—	36	36½	36¾	36½
Methylene blue ..	4¼	—	5½	4½	5½	4½

Ultramarine, owing to its peculiar character, presents difficulties in manipulation. Numerous determinations of its copper-content were made, but in the opinion of the Sub-Committee these results were not in sufficiently close agreement. Further work will be carried out on this colouring material and a supplementary Report will be published later.

APPENDIX

LIST OF REAGENTS

(1) *Ammonium citrate solution*: 10 g. of ammonium citrate are dissolved in distilled water and diluted to 100 ml.

(2) *Concentrated ammonia*: sp.gr. 0·880.

(3) *Sodium diethyldithiocarbamate solution*: 0·1 g. of pure sodium diethyldithiocarbamate is dissolved in distilled water and diluted to 100 ml.

(4) *Gum arabic solution*: 5 g. of gum arabic are dissolved in about 80 ml. of distilled water, the solution is filtered, and the filtrate is diluted to 100 ml.

(5) *Dilute hydrochloric acid*: 1 volume of concentrated hydrochloric acid (sp.gr. 1·16) is mixed with 3 volumes of distilled water.

(6) *Standard copper solution*:

Solution A.—0·3928 g. of pure copper sulphate ($CuSO_4.5H_2O$) is dissolved in distilled water, 1 drop of concentrated sulphuric acid is added, and the solution is diluted to 1000 ml. This solution may be retained as a stock solution; 1 ml. of this solution = 0·0001 g. Cu.

Solution B.—One volume of solution A is diluted to 10 volumes with distilled water; 1 ml. of this solution = 0·00001 g. Cu. (Solution B should be freshly prepared as required.)

(7) *Filter-papers.*—Before use the filter-papers are washed with dilute hydrochloric acid and then with distilled water.

The determination of copper is carried out on the acid-alcohol-water filtrate obtained from the filtration of the lead sulphate (see Second Report—The Determination of Lead—ANALYST, 1935, **60**, 541–552).

METHOD

The acid-alcohol-water filtrate from the lead sulphate precipitation is diluted with water to 100 ml. An aliquot portion of the solution (or the whole of the filtrate without previous dilution) is transferred to a 100-ml. Nessler cylinder, and 5 ml. of ammonium citrate solution are added. The solution is then neutralised with concentrated ammonia and 2 ml. of this reagent are added in excess. One ml.

of the gum arabic solution is added, and the solution is cooled and diluted to 100 ml. with distilled water.

A series of standard comparison solutions is prepared, each containing in 100 ml. 2 ml. of ammonia, 5 ml. of ammonium citrate solution and 1 ml. of gum arabic solution, together with different amounts of standard copper solution (Solution B).

The test solution and standards should be water-white. Each solution is mixed with 2 ml. of sodium diethyldithiocarbamate solution, and the test solution is matched against the standard comparison solutions. The volume of the aliquot portion of the test solution taken for colorimetric determination of the copper should be such that the colour produced with sodium diethyldithiocarbamate solution is matched by a standard comparison solution containing not more than 10 ml. of standard copper solution B.

In order to determine the copper in the reagents (which should be "copper-free") a blank experiment is carried out on the same quantities of reagents as are used in the test and in the preliminary treatment, the procedure throughout being exactly as described above for the determination of total copper in food-colouring materials.

If the acid-alcohol solution is opalescent or contains iron in sufficient amounts to interfere with the colorimetric determination of the copper (as shown by the appearance of a slight greenish-yellow colour in the solution on the addition of ammonium citrate), the remaining aliquot portion of the acid-alcohol solution (or a freshly prepared one) should be treated as follows:

The solution is neutralised with ammonia, 5 ml. excess being added, and boiled for two or three minutes. It is then filtered through a folded filter-paper (similar in texture to Whatman No. 1), and the filter is washed with water. The residue on the paper is dissolved in 5 ml. of dilute hydrochloric acid, the solution is diluted slightly with water, and the iron is precipitated and filtered as before. The residue is washed with water and the combined ammoniacal filtrates and washings are cooled and made up to 100 ml. in a measuring flask.

This solution, or an aliquot portion, is then tested colorimetrically for copper as before, without the addition of ammonium citrate.

NOTES.—(1) In the case of samples for which the arsenic-content is not required, the solution obtained by wet oxidation (The Determination of Arsenic, ANALYST, 1930, **55**, 102–9), is not treated for removal of arsenic by the distillation method, but is almost neutralised with ammonia and directly treated with hydrogen sulphide, etc., exactly as described in the Second Report.

(2) Throughout the determination care should be taken to prevent contamination of the test solution by traces of metal derived from copper appliances, *e.g.* Bunsen burners, door and cupboard handles, taps, etc.

For and on behalf of the Sub-Committee,

(*Signed*) T. MACARA (*Chairman*)
S. G. CLIFFORD (*Hon. Sec.*)

April, 1939

Erratum.—A VOLUMETRIC METHOD FOR THE DETERMINATION OF SULPHUR, March issue, p. 182, line 1. *For* 0·1622 molar *read* 0·01622 molar.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DESTRUCTION OF DILUTE OIL HYDROSOLS IN VOLUMETRIC ANALYSIS

When a mixture of two organic liquids, only one of which is soluble in water, is added to water, the insoluble liquid is frequently precipitated in the form of a dilute oil hydrosol, which is a dilute unstabilised emulsion of the water-in-oil type. Such hydrosols are also obtained when oils are shaken with water. These systems are of great stability and are opaque—facts of importance when it is desired to perform a volumetric determination upon the aqueous phase in the presence of an internal indicator.

Up to the present, the standard method for the destruction of hydrosols has consisted in the addition of electrolytes. The oil globules bear negative charges, and the addition of cations brings about their eventual coagulation. Such a process, however, is extremely slow, even when the mobile hydrogen ion or the quadrivalent thorium ion is employed. Moreover, the use of electrolytes may well be prohibited by the nature of the analysis.

Cataphoretic methods may also be utilised for the destruction of hydrosols. Unless, however, very high potential gradients are employed, such procedures are too tedious to be practicable.

The method evolved in this laboratory is simple, rapid, and apparently infallible. It involves merely the agitation of the hydrosol with about one quarter of its volume of one of the partially soluble alcohols (*e.g.* amyl alcohol). These alcohols have low interfacial tensions with respect to water. On shaking with hydrosols they form fine emulsions, in which the dispersed oil is brought into intimate contact with, and dissolved by, the alcohol. When the shaking is discontinued, the alcohol and the dissolved oil rise to the surface, leaving the aqueous phase quite clear.

When a water-soluble component is to be extracted from an organic liquid, the formation of a hydrosol may be inhibited by the addition of amyl alcohol to the liquid before the extraction. The optimum proportion of alcohol for a given system must be determined experimentally.

The use of ether in place of the higher alcohols has been found to be advantageous in many instances. That liquid is difficult to emulsify, but the disadvantage tends to be nullified by its low density and its high solvent power.

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March, 1939

WATER ANALYSIS: EFFECT OF SUSPENDED MATTER AND DAYLIGHT ON INCUBATION TESTS

The Royal Commission on Sewage Disposal in their Eighth Report recommend the dissolved atmospheric oxygen absorbed ("B.O.D.") test as a standard, and direct that the test should be carried out on the shaken-up sample so as to include the suspended matter.

The Ministry of Health official *Methods of Sewage Analysis*, which were based largely on the work of the Royal Commission, also direct that the albuminoid ammonia and permanganate tests should be carried out on the shaken-up sample, but it is to be noted that this publication specifically applies to "sewage and sewage effluents," in which, presumably, the suspended solids are of fairly constant composition.

If, however, there is much suspended matter present, or if it varies much in character, the albuminoid ammonia and permanganate figures obtained from turbid unfiltered samples may be very misleading, and erroneous conclusions will be drawn from such figures unless they are correlated with the actual amount of suspended matter present. If trustworthy opinions are to be drawn from the analysis of samples containing much suspended matter, they can be secured only by differentiating between dissolved and suspended matter.

This applies particularly to samples of river water, as not only may the suspended matter vary considerably in character, but its amount will vary greatly according to the method, depth and place of sampling. More suspended matter will be found near the bank or bed of the stream than near the middle of the surface water; eddies may also cause variations in turbidity.

Ammonia and permanganate figures from the turbid sample will naturally vary with the amount of suspended matter included in the sample, but they would not represent any real difference in the quality of the actual water.

Again, albuminoid ammonia and permanganate figures obtained from a water containing much suspended solids have a significance entirely different from that which would be attached to the *same figures* if obtained from a clear water.

It might be thought that the "B.O.D." test, which measures de-oxygenating power, could be relied upon to give a trustworthy indication of the character of a turbid water, but this is by no means so, and the following series of tests on some samples of river water show that this test may, in certain circumstances, prove very unreliable if applied to the turbid, unfiltered waters.

"B.O.D." TEST

		Results in parts per 100,000		
Sample No.	When taken	Filtered Incubated in the dark	Unfiltered Incubated in the dark	Unfiltered Incubated in daylight
1	June	0·34	0·77+x	−4·9
2	July	0·16	0·83+x	−2·8
3	,,	0·34	0·57	−2·6
4	,,	0·39	0·81+x	—
5	,,	0·26	0·74+x	—
6	Sept.	—	—	−1·6
7	,,	—	0·6	−1·75
8	Oct.	—	0·11	−1·55

The "+x" sign indicates that all the dissolved oxygen had disappeared; the minus sign indicates, on the other hand, that not only was there *no oxygen absorption*, but there was actual oxygen *production* up to a considerable degree of supersaturation. This was, of course, due to algal activity during the hours of daylight. There were no algae present in November and December samples, nor were there any supersaturation phenomena.

Of the above samples, Nos. 1, 2, 3, and 7 were coloured by abundant growths of algae; Nos. 6 and 8 contained the merest trace of suspended matter and algae were not visible in the samples when taken, but at the end of the 5-day incubation period, algal growth was very evident.

The foregoing results indicate the extreme care that is necessary in differentiating between clear and turbid samples of water, and it would seem that "B.O.D." figures ranging from complete de-oxygenation on the one hand to supersaturation on the other could be obtained merely by varying the amount of daylight admitted to the incubator.

This phenomenon of oxygenation arising from algal activity is fully recognised in the Metropolitan Water Board's reports, and is one that should be realised by all engaged in water analysis. HERBERT F. STEPHENSON

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February, 1939

THE PRESERVATION OF SODIUM RHODIZONATE INDICATOR PAPER

OUR experience with the titration of sulphates in solution by means of barium chloride, using the sodium salt of rhodizonic acid as indicator, confirms that of Kocher (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 331), who has found that the indicator is best used externally. For this purpose it is conveniently "spotted" on filter-paper, about half-a-dozen spots being made for a titration.

Our interest in this titrimetric method is in the determination of gypsum in mine dusts stone-dusted with this inert dust (*Safety in Mines Research Board Paper*, No. 101, 1938). When, for such analyses, a large number of samples enter the laboratory together, it would be convenient to prepare sufficient solution of the indicator, or a sufficient number of "spotted" filter-papers for, say, a day, so that the large number of titrations may be done expeditiously. The preparation of the indicator in bulk, however, is not possible, for the solution gradually fades and does not keep for a day, and the spots on the filter-paper fade even more rapidly—in the course of an hour or even less.

The rapid fading of the spots appears to be due to oxidation of the rhodizonic acid when moist, for the following procedure considerably prolongs their life. Strips of filter-paper are "spotted" with 0·1 per cent. sodium rhodizonate solution and dried in an evacuated desiccator over calcium chloride. When dry, the papers are still effective after a day or more, even when in contact with the air. If they are preserved *in vacuo* they remain effective for several days.

By this simple method a large quantity of the filter-paper may be prepared and the annoyance of having to prepare it before each titration is eliminated.

A. L. GODBERT
R. BELCHER

SAFETY IN MINES RESEARCH BOARD LABORATORIES
SHEFFIELD
February, 1939

THE PROPORTION OF COPPER IN TOMATO PURÉE

SAGE and Stevens (ANALYST, 1938, **63**, 719), referring to the paper by Cockburn and myself (ANALYST, 1938, **63**, 482), pointed out that the final solution, after being made ammoniacal, must be perfectly colourless, and suggested the use of ammonium oxalate during the final stages of the destruction of the organic matter.

In this laboratory very little difficulty has been experienced in obtaining a colourless ammoniacal solution, but when a yellow sulphuric acid solution was obtained the addition of ammonium oxalate was of no assistance and a fresh determination was made. As a rule this proceeded in a satisfactory manner.

The exact conditions for the production of a colourless solution have been ascertained in experiments with lard, as it seems to be established that substances containing a high proportion of fat are particularly liable to give trouble. The quantities of material and reagents were of the order of those used in the determination of copper in tomato purée (*loc. cit.*). It was found that a coloured or a colourless solution could be produced at will. The essential conditions for obtaining a solution free from colour are rapid heating of the sulphuric acid and rapid and continuous addition of the nitric acid.

The details of the method of destruction are as follows:—Three g. of lard were introduced into a 300-ml. Kjeldahl flask, together with 5 ml. of water and 5 ml. of conc. nitric acid. The contents of the flask were heated, with continuous shaking, over a naked flame until they began to turn brown. After cooling, 10 ml. of conc. sulphuric acid were added slowly over a period of 3 minutes. The flask was then placed upright on a piece of duralite with a 2-inch hole and heated strongly. Simultaneously, conc. nitric acid was dropped in at the rate of 10 ml. per minute. In about 1½ to 2 minutes the colour of the solution became clear bright yellow. The addition of nitric acid was discontinued, the flask was cooled, 30 ml. of water were added, and the solution was boiled until copious fumes appeared. The boiling sulphuric acid at this stage was quite colourless and showed no trace of colour after being cooled, diluted and made ammoniacal.

The foregoing method invariably yields a colourless solution, but as there is a possibility of loss, due to spurting, during the rapid addition of nitric acid, the following procedure for the removal of interfering yellow colour may be preferred. The yellow ammoniacal solution is transferred to a separator, 10 ml. of sodium diethyldithiocarbamate solution are added, and the mixture is extracted with four successive quantities of chloroform (10, 5, 5 and 5 ml.). The united chloroform extracts are evaporated in a Pyrex test-tube (6″ × 1″) and the dry residue is heated for 1 minute with 1 ml. of conc. sulphuric acid. Five drops of conc. nitric acid are added, and the heating is continued until oxides of nitrogen have been expelled. Five ml. of water are then added, and the liquid is evaporated until fumes appear, after which it is diluted, rendered ammoniacal, filtered through an acid-extracted paper, and made up to a definite volume. The solution is perfectly colourless.

Copper equivalent to 10 ml. of the standard solution (0·0001 g.) is completely extracted by shaking four times with chloroform, as described above.

MAGNUS HERD

CHEMICAL AND CITY ANALYST'S DEPARTMENT
20, TRONGATE, GLASGOW, C.1

March, 1939

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY

V. NITROUS FUMES*

THE situations in which nitrous fumes may be encountered in dangerous concentrations include ammonium nitrate works, celluloid works, dyestuffs works, explosives works, nitric acid works, nitrocellulose paint, lacquer and leather cloth works, photographic film works and sulphuric acid works (chamber process). They are also encountered in electro-plating, engraving, metal cleaning and photogravure processes, and are formed during oxyacetylene welding, particularly when an oxyacetylene flame plays on cold steel in a confined space. They have caused fatalities during the heat treatment of metals in molten nitrates.

POISONOUS EFFECTS.—There may be, and generally are, no immediate effects, and therefore it is impossible to foretell the serious consequences that may result from the inhalation of these fumes. A workman, unaware that he has inhaled the fumes, continues at work, often remaining well until after he has returned home. Some hours later he becomes restless with a dry cough and shortness of breath. These symptoms increase, accompanied by a frothy sputum, tinged with blood. If appropriate treatment is not applied, death follows from oedema (water-logging) of the lungs. The following table, based on various authorities (*e.g.* Henderson and Haggard, *Noxious Gases*, 1927; International Labour Office, etc.), shows the results following the inhalation of nitrous fumes in various concentrations:

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* Leaflet No. 5. H.M. Stationery Office, York House, Kingsway, London, W.C.2. March 14th, 1939. Price 3d. net.

Parts by vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 100,000	0·03	Maximum concentration allowable for an exposure of several hours' duration.
1 in 10,000	0·3	Only sufficient to produce mild irritation of the throat and chest, but dangerous to inhale for only a few minutes.

At concentrations higher than 1 in 10,000 the fumes are frequently fatal if breathed for more than a few minutes. Hence any atmosphere in which nitrous fumes are noticeable by odour, irritating effects or colour should be regarded as dangerous.

METHODS OF DETECTION.—Starch and potassium iodide papers are fairly sensitive to low concentrations of nitrous fumes, but owing to their lack of specificity and to the difficulty of obtaining complete absorption of the gas by the paper, their use was not considered as a standard test.

Two tests, which depend on the diazo reaction, are specific for nitrous fumes and are very sensitive; they are: (i) the Griess-Ilosvay reaction; (ii) the Bismarck Brown test. In the former the gas is bubbled through a solution of α-naphthylamine and sulphanilic acid in acetic acid, a rose-pink colour being produced; in the latter test the gas is bubbled through a solution of *m*-phenylenediamine hydrochloride in acetic acid, and an orange colour, due to the formation of Bismarck Brown, is produced. As the Griess-Ilosvay test is somewhat more sensitive than the Bismarck Brown test, it was adopted as the standard test. It is sufficiently sensitive to be capable of detecting nitrous fumes at a concentration of 1 part in 100,000. The test is made by drawing the atmosphere under examination through a tube containing the reagent by means of a hand-pump until a rose-pink colour of standard depth is reached. From the number of strokes of the pump required to produce the standard colour, the concentration of nitrous fumes present can be obtained by reference to a table given in the Leaflet.

INSTRUCTIONS FOR CARRYING OUT THE TEST.—Under Regulation 7 of the Chemical Works Regulations, 1922, the test shall be carried out only by a responsible person appointed by the occupier, and all necessary steps shall be taken for the protection of that person. When testing the concentration of nitrous fumes inside a tank prior to the entry of a workman, one test may be insufficient; if there is a chance of the concentration inside the tank rising, the atmosphere must be sampled at intervals throughout the period of work.

Apparatus.—The hand-pump used for sampling the atmosphere has a barrel of approximately 1·25 in. bore and a capacity of 126 ml. It is fitted with a nozzle opening for attaching rubber tubing, and, if desired, may be provided with a device for counting the number of strokes made. A convenient type of pump is described (*cf.* Leaflets Nos. 1 and 2, ANALYST, 1937, **62**, 607; 1938, **63**, 658).

The sample is drawn through the reagent contained in a bubbler consisting of a side-arm test-tube of approximately 0·75 in. internal diameter, and about 6 in. in length, fitted with a rubber bung through which passes a delivery tube (approximately 0·125 in. bore) reaching nearly to the bottom of the test-tube and terminating in a fine jet. It is convenient to calibrate the test-tubes to avoid measuring out the reagent each time a test is made. The bubbler is mounted on the barrel of the pump in such a way that the reagent is easily seen, and the tube readily removable, for comparison with the standard and replacement by a fresh tube.

A convenient arrangement of the apparatus is described and illustrated in the Leaflet.

Preparation of Reagent.—(*a*) 0·5 g. of sulphanilic acid is dissolved, with slight warming, in 150 ml. of a solution of 70 ml. of glacial acetic acid in 500 ml. of water. (*b*) 0·1 g. of α-naphthylamine is boiled for a few minutes, in 20 ml. of water, and the mixture is poured into 150 ml. of a solution of 70 ml. of glacial acetic acid in 500 ml. of water. (*c*) *Immediately before the test is made* 5 ml. of each of the solutions (*a*) and (*b*) are mixed in the bubbler.

The solution should remain colourless after mixing; if any pink colour is developed the solution must be discarded and a fresh portion of reagent measured out.

Preparation of Standard Colour.—(*a*) 0·1 g. of dimethylamino-azo-benzene (of reagent quality) is dissolved in acetone, and the solution is made up to 100 ml. with acetone (of reagent quality) in a graduated flask—Solution A. (*b*) Five ml. of Solution A are made up to 250 ml. with acetone—Solution B. This solution must be kept in a stoppered bottle in the dark. (*c*) When required, the standard colour is prepared as follows:—One ml. of Solution B is pipetted into a tube of diameter equal to that of that of the side-arm test-tubes used for the test, and made up to 10 ml. with dilute (approximately 7 per cent.) hydrochloric acid. The standard, when not in use, must be well corked or sealed and kept in the dark.

Method.—The strokes with the hand-pump are made very slowly (approximately 10 seconds per stroke), and the pumping is continued until the depth of colour developed is a little less than that of the standard colour (the number of strokes made being counted). The bubbler is then removed, and *after 2 minutes* (to allow of full development of the colour) it is compared with the standard tube, the two tubes being observed side by side by transversely transmitted daylight. If the colour given in the test is less than that of the standard, the bubbler is replaced and further strokes of the pump are made until exact equivalence is obtained after a standing period of 2 minutes.

The following table shows the number of strokes necessary for various ranges of concentration in order to obtain the standard depth of colour:

Concentration	Number of strokes
Above 1 in 8,000	Less than 1
1 in 8,000 to 1 in 13,000	1 to 2
1 in 13,000 to 1 in 20,000	2
1 in 20,000 to 1 in 27,000	3
1 in 27,000 to 1 in 35,000	4
1 in 35,000 to in 45,000	5
1 in 45,000 to in 55,000	6
1 in 55,000 to in 65,000	7
1 in 65,000 to in 75,000	8
1 in 75,000 to in 85,000	9
1 in 85,000 to in 100,000	10

Under certain conditions a cloudiness may be produced in the test solution, but this does not interfere with the comparison with the standard colour.

Directions are given for a procedure for sampling the air from a space that is not readily accessible or where there is a possibility of highly toxic concentrations of nitrous fumes being present, *e.g.* in acid tanks.

First Aid.—Full details of the treatment of cases of gassing are given in Factory Form No. 395 (H.M. Stationery Office, price 1d. net). As there is invariably a delay of some hours before serious symptoms may develop, strict confinement to bed for not less than two days is advisable.

The National Physical Laboratory

REPORT FOR THE YEAR 1938*

THE Executive Committee record their regret at losing the services of Dr. W. L. Bragg, O.B.E., F.R.S., as Director of the Laboratory, on his appointment as Cavendish Professor of Experimental Physics in the University of Cambridge. They wish to express their pleasure at the appointment, by the Lord President of the Council, of Dr. C. G. Darwin, M.C., F.R.S., lately Master of Christ's College, Cambridge, as successor to Dr. Bragg.

ASSISTANCE TO INDUSTRY.—The present Report contains many examples of researches having application to specific problems that arise in industry. Apart from such items, the Laboratory includes in its programme a number of broader investigations which affect the well-being of the community as a whole or are of interest to industry in general. Architectural acoustics and accurate gauging are examples of this type of work.

The Report gives a brief summary of the more important investigations completed during 1938, and also describes work carried out on behalf of various Government Departments and research organisations. Some of the results summarised in the reports of the work of the several departments include the following:

NOISE MEASUREMENT.—The "standard" and "portable" noise meters designed at the Laboratory are finding further outlets for specific applications. The problem of silencing the motor cycle is now being undertaken by the Laboratory on behalf of the Institution of Automobile Engineers and the Mechanisation Board.

INTERNATIONAL TEMPERATURE SCALE.—The method employed by the Laboratory for determining the freezing-points of palladium and platinum has now been extended to rhodium. A good example of the use of fixed points as secondary standards is the establishment of the scale of colour temperature by means of lamps calibrated on black-body radiators at the freezing-points of platinum (1773° C.), rhodium (about 1965° C.), and iridium (about 2450° C.). (*Cf.* ANALYST, 1938, **63**, 343.)

X-RAY AND GAMMA-RAY INTENSITY AND PROTECTION.—It has been found that the röntgen, as now defined, is a suitable unit of quantity for the measurement both of X-rays and gamma-rays. The use of barium concrete and similar substances as protective materials in the X-ray departments of hospitals has made it desirable that their protective properties, as compared with lead, should be accurately known. The results obtained indicate that the lead equivalent of a material can now be calculated for X-rays of any practical voltage with an accuracy sufficient for medical purposes.

TOOTH STRUCTURE.—Work on the relationships between the selective orientation of the crystallites of the enamel of human deciduous teeth and the prism structure revealed by the microscope has been completed. It has been found that each prism is composed of a large number of submicroscopic crystallites of apatite, which consist of two groups so arranged that their axes make angles of approximately 5° and 40° with the direction of the prism. The main constituent of the enamel is hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, in which a small percentage of the calcium atoms is replaced by magnesium.

COMMERCIAL COLOUR-MATCHING LAMPS.—With modern improvements in artificial daylight lamps it has been found that some of the better types of lamp are preferable to light from an overcast north sky. Inferior types of colour-matching lamps, however, are liable to give results differing widely from those obtained with any kind of daylight. The colour-matching properties of a lamp are determined by the shape of the curve which shows how the radiant energy is distributed over the spectrum, and at present it is not practicable to measure the spectral energy distributions of commercial lamps. Before an investigation can be made it is necessary to have some standard of spectral energy distribution for comparison. Any form of daylight is unsuitable, and "Illuminant C," one of the standard sources adopted by the International Commission on Illumination in 1931 for employment in colorimetry, was therefore selected. Specimens of different spectral absorptions which matched under "Illuminant C" were illuminated by the commercial lamps under examination, and the differences were measured. A figure of merit representing the colour-matching performance of the lamp was derived from the average colour difference for a large number of pairs of specimens. In this test, lamps fell into two fairly well-defined groups—those which resembled north sky light both in colour and in colour-matching properties, and those which resembled it in colour only. As this procedure is too long and expensive for a routine test under a specification, search was made for a simpler test that would grade the lamps in much the same way. If brightness comparisons are made by means of a series of monochromatic gelatin filters to filter the light from both sources, a curve can be drawn which gives a rough representation of the trend of the spectral energy distribution curve of the lamp relative to that of "Illuminant C." This simplified test has been recommended to the Technical Committee of the British Standards Institution as suitable for a specification. It is sufficiently simple to be applicable in industrial laboratories.

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 2s. 6d. net.

TESTS ON PHOTOGRAPHIC LENSES.—It is often not realised by professional photographers that the use of a small stop lowers the standard of definition. The belief that a small stop is necessary to secure a sharp picture doubtless dates from early days when the best lenses fell far short of the standard customary to-day. To eliminate the personal factor in visual tests of lenses, the universal lens interferometer is used. With this instrument the light which passes through the lens is made to give a direct indication of the errors present. The principle employed is that if light from a given source is divided into two portions, as by partial reflection and partial transmission at a lightly silvered glass surface, and the two beams are subsequently re-united, any progressive lagging of one beam behind the other causes alternate light and dark bands or "fringes" to be seen instead of a uniformly bright area. The change from a light to a dark band corresponds with a variation in the distance to the focus of about an eight-thousandth of a millimetre. These bands can be easily counted and, if desired, may be photographed.

STATIC ELECTRICITY IN DRY-CLEANING PROCESSES.—In a previous investigation (*cf.* ANALYST, 1937, **62**, 462; 1938, **63**, 344) it was shown that the risk of fire and explosion due to the generation of static electricity in dry-cleaning processes was greatly reduced by the use of special soaps. A portable instrument capable of showing if the conductivity of a cleaning solvent is adequate has now been devised.

PHOTOMETRIC STANDARDS.—A procedure consistent with the visibility curve was formally adopted in 1937 by the International Committee of Weights and Measures. In this procedure a blue-tinted glass is inserted between the photometer head and the lamp of lower colour temperature so as to obtain in the photometer field as close a colour match as possible with the lamp of higher colour temperature. The transmission factor of this glass is calculated from spectro-photometric measurements. This new procedure necessitates a complete re-measurement of the substandards used at the Laboratory (*cf.* ANALYST, 1938, **63**, 344).

REFRACTORY MATERIALS.—*Seger Cones.*—At the request of the British Refractories Research Association an investigation of the "squatting points" of seger cones, covering a range of temperature from about 1560° C. to 1760° C., has been made. It has been found that the cones, when properly used, allow of the measurement of temperature over this range with a precision that is little inferior to that of a good optical pyrometer.

ANALYTICAL METHODS IN METALLURGY.—In pursuance of the programme of work on the accurate determination of oxygen, nitrogen and hydrogen in steel, the efficiency of the vacuum fusion method has been tested by means of steel capsules containing known weights of various oxides and silicates. The results show that, at the high temperature employed, all of these are quantitatively reduced. The method has also been used with success to determine the oxygen-content of films on the surface of steel sheet. Work on the iodine method has been mainly devoted to the examination of three steels containing varying proportions of sulphur and phosphorus. A sample of pure iron has been used for comparison, with the object of ascertaining if a blank must be allowed.

Microchemical methods of quantitative analysis have been applied in a number of instances arising from work in this and other Departments of the Laboratory. These methods are of special value in examining segregation in ingots or castings. Several small pieces of laboratory apparatus have been designed in the course of the work. Special attention has been given to the determination of the total carbon in small samples of ferrous materials by combustion, and of very minute quantities of carbon in purified iron and its alloys. Rollet's colorimetric method of determining small amounts of nickel has been investigated and modified to give greater accuracy.

The quartz spectrograph has been used mainly for qualitative analysis, but a series of analysed specimens of copper containing added elements is being employed in determining the limits of accuracy obtainable in quantitative spectrographic analysis.

International Union of Chemistry

NINTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE Report covers the year ended September 30th, 1938. Only one change has been made in the Table, the atomic weight of phosphorus having been changed from 31·02 to 30·98.

CARBON.—Moles and Escribano (*Compt. rend.*, 1938, **207**, 66) have redetermined the densities of oxygen and carbon dioxide at different pressures. From the results they calculate the molecular weight of carbon dioxide to be 44·007 and the atomic weight of carbon 12·007.

PHOSPHORUS.—Hönigschmid and Menn (*Z. anorg. Chem.*, 1937, **235**, 129) have compared phosphorus oxychloride with silver and silver chloride. Commercial oxychloride was warmed with phosphorus pentoxide to remove pentachloride and fractionally crystallised to remove trichloride, after which it was subjected to a series of distillations with fractionation columns in exhausted glass systems which provided for removal of head and tail fractions. The samples for analysis were sealed in glass balls, which were weighed in air and in water and broken under ammonia solution in a sealed glass flask. The average value from head fractions was 30·978, and that from the middle fractions 30·979. Tail fractions gave slightly higher values, diminishing as the fractionation proceeded. The authors believe that 30·978 represents the best value from their work. This value agrees closely with that found from the density of phosphine by Richie (Report for 1930). From these and other considerations it seems to be certain that the international value 31·02 is too high, and the atomic weight in the Table has therefore been changed to 30·98.

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* Authors of papers bearing on the subject are requested to send copies to each of the four members of the Committee:—Professor G. P. Baxter, Coolidge Laboratory, Harvard University, Mass., U.S.A.; Professor M. Guichard, Faculté des Sciences, 1, Rue Victor-Cousin, Paris; Professor O. Hönigschmid, Sophienstrasse 9/2, Munich; Professor R. Whytlaw-Gray, The University, Leeds.

Europium.—Baxter and Turner (*J. Amer. Chem. Soc.*, 1938, **60**, 602) have published further details on the analysis of europous chloride. Comparison with silver gave results for the atomic weight of europium, ranging from 151·954 to 151·963. Kapfenberger (*Z. anorg. Chem.*, 1938, **238**, 273) also analysed europous chloride obtained from a rare earth fraction consisting chiefly of samarium and gadolinium salts; the values for the atomic weight ranged from 151·895 to 151·911. The discrepancy between these two sets of determinations is presumably to be explained on the basis of impurity in one or both samples. Because of these and other discrepancies no change in the atomic weight of europium is made in the Table.

Lead.—Nier (*J. Amer. Chem. Soc.*, 1938, **60**, 1571) has found the isotopic composition of common lead to vary over a considerable range, although the atomic weight (computed from isotopic abundances) diverges appreciably from the international value 207·21 only in one instance out of ten, that of lead from Joplin, Mo., U.S.A. (from galena I, 207·178; from galena II, 207·175). The value 207·21 is retained for the Table, although in future it is apparent that the geological occurrence of common lead must be taken into account so far as its atomic weight is concerned.

Egypt

REPORT ON THE WORK OF THE CHEMICAL LABORATORY, MINISTRY OF JUSTICE, FOR THE YEARS 1929–1934

In 1920 a small laboratory was established for the work of the Medico-Legal Department, but its duties were confined to the detection of poisons in viscera and in human and animal secretions, to the examination of exhibits in criminal cases, and to the investigation of certain narcotics. At first only two chemists were engaged in the work; there are now nine. The Director is Mr. F. Bamford, B.Sc. In 1921 the number of exhibits examined was 903; by 1929 this number had increased to 12,570. Since 1934 difficulties tending to delay the reports of investigations have been overcome.

Illicit Traffic in Narcotics.—The history of the Laboratory has been closely associated with the illicit traffic in narcotic drugs. At first this traffic was mainly concerned with opium, hashish and manzoul, and it was not until about 1924 that the "white poisons" appeared in Egypt. In that year there were examined in the Laboratory 11 samples of heroin, 105 of morphine and 148 of cocaine. The popularity of cocaine lasted for only a year or two, and in 1926 it was almost completely replaced by heroin, the trade in which is more profitable. In 1929 the number of samples of this kind reached almost 20,000, but by 1934 the trade in "white poisons" had decreased, their place having been taken by manzoul.

Composition of Manzoul.—Manzoul, the properties of which are similar to those of hashish, is of a more complicated composition than formerly. At one time it consisted largely of hashish, but now this is being replaced to an increasing extent by muscat nut in admixture with certain alkaloids. The danger of eating muscat nut is as yet only imperfectly realised; when taken in large quantities it produces serious symptoms which may prove fatal.

Human Poisoning Cases.—The poison most extensively used is arsenic, whilst mercury, strychnine and aconite have been detected in a number of cases.

There has been an increase in the suicide cases; the poisons used have included morphine, strychnine, phosphorus, phenol, mercury and arsenic.

The method of preparing viscera for analysis devised by the Director of the Laboratory (*cf.* Bamford, ANALYST, **1938**, **63**, **645**) is now in regular use.

Suicide with Carbon Tetrachloride.—A British soldier killed himself by swallowing carbon tetrachloride which had been supplied for cleaning clothes. As a result of this case, representations were made to the Commander of the British Army through the Consul General, pointing out the danger attending the use of carbon tetrachloride, and the necessity of labels for bottles containing it, with an indication of its poisonous properties. As a result, another cleaning agent was substituted for carbon tetrachloride and a distinctive label was affixed to bottles containing it.

APPROXIMATE DATE OF THE USE OF FIREARMS.—An investigation was made in the Laboratory as to the possibility of ascertaining the approximate date at which a firearm had been discharged. It was hoped at first that it might be possible to form an opinion on this point by comparing the relative quantities of potassium carbonate and bicarbonate left in the barrel, but it was soon found that the result was affected by the various conditions to which the firearm was exposed after firing. These factors included the condition of the firearm before firing and in the interval before it was found by the police, and the degree of moisture in the air. Different results were obtained in winter and in summer. The experimental work was therefore discontinued.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

New Constant for Olive Oil. J. Grossfeld and H. Timm. (*Z. Unters. Lebensm.*, 1939, 77, 249–253.)—In an investigation of the adulteration of edible oils with mineral oil by a method specially designed for the purpose (Grossfeld, *Z. Unters. Lebensm.*, 1936, 72, 422) it was found that the small amount of mineral oil or hydrocarbons apparently present was always greater in olive oil than in other edible oils, and the results point to the presence in olive oil of a naturally occurring hydrocarbon. Such a hydrocarbon was shown to be present by Thorbjarnarson and Drummond (ANALYST, 1935, **60**, 23), who identified it with squalene, which differs from the mineral paraffin oils in its high degree of unsaturation corresponding with an absorption of 12 atoms of iodine and a theoretical iodine value of not less than 371. Bolton and Williams (ANALYST, 1930, **55**, 5) have shown that olive oil may be distinguished from other edible oils by the iodine value (Hübl or Rosenmund-Kuhnhenn, but not Wijs) of the unsaponifiable portion. Loew (*Olii minerali, Olii grassi, Vernici*, 1931, **11**, 9–10) has found that the unsaponifiable fraction of olive oils from different sources has an iodine value ranging from 125 to 168, whilst in other oils the range is 96 to 130. Ricca and Lamonica (*ibid.*, 1932, **12**, 73) found values of 60 to 134 for Calabrian olive oil, so that the use of this value presents difficulties. It appeared a promising method to express the iodine value of the unsaponifiable matter, not on the unsaponifiable fraction, but on the original oil. A comparison of the methods of Hanus and Margosches for the determination of the iodine value showed that the latter method is the more suitable for the purpose. The iodine value of the unsaponifiable fraction, when converted by calculation to a "crude squalene" figure expressed as a percentage of the original oil, proved to be a useful constant to distinguish olive oil from other edible oils. The procedure is as follows:—The oil (5 g.) is saponified beneath a reflux condenser with 3 ml. of 47 per cent. potassium hydroxide solution (sp.gr. 1·5) and 20 ml. of 90 per cent. alcohol. When cold, the liquid is shaken with 50 ml. of petroleum spirit (b.p. 60 to 70° C.) until a homogeneous mixture is formed. Water (20 ml.) is then added, and mixing is effected by repeated inversion of the vessel, violent shaking being avoided, and the mixture is allowed to separate overnight. As described in an earlier work (*Z. Unters. Lebensm.*, **1938**, **76**, 521), 25 ml. of the petroleum spirit layer are evaporated, and the residue is dried at 105° C. and weighed. The weight of the residue, multiplied by 35·2 (which includes a factor, *viz.* 0·88 compensating for the reduction in volume of the petroleum spirit layer), gives the percentage of hydrocarbons in the oil. The residue is dissolved in 2·5 ml. of alcohol at 50° C., a slight turbidity being disregarded. The solution is treated with exactly 5 ml. of $N/5$ iodine solution (Margosches) and mixed by gentle shaking. Water (50 ml.) is added immediately and, after being mixed, the liquid is allowed to stand for 3 minutes, after which it is titrated with $N/10$ sodium thiosulphate solution and the result is deducted from that of a blank determination. The percentage of crude squalene in the oil is obtained by multiplying the iodine absorption figure (ml. $N/10$) by 0·120, which includes the correction for the reduction of the volume of the petroleum spirit layer previously mentioned. From four samples of olive oil the following figures were obtained:—(1) hydrocarbons, per cent., 0·63 to 0·99; (2) crude squalene, per cent., 0·41 to 0·54. For some other edible oils the corresponding figures were:—rape oil, (1) 0·48, (2) 0·05; arachis oil, (1) 0·33, (2) 0·07; apricot kernel oil, (1) 0·25, (2) 0·02; an edible oil, (1) 0·13, (2) 0·06; cod-liver oil, (1) 0·30, (2) 0·05. With old, rancid olive oil the figures were of the same order as those obtained with the other edible oils mentioned above, and the method is therefore applicable only to fresh samples of olive oil.

A. O. J.

Seed and Fruit-coat Fats of *Celastrus paniculatus*. B. G. Gunde and T. P. Hilditch. (*J. Chem. Soc.*, 1938, 1980–1985.)—*Celastrus paniculatus* is a large deciduous shrub which grows in India. The oil from the seeds is used medicinally in rheumatic diseases. Both the seed and fruit-coat fats contain appreciable amounts of formic, acetic and benzoic acids in addition to the higher fatty acids (palmitic, stearic, oleic, linolic and linolenic). The seed-fat, a greenish-brown liquid at room temperature, had the following characteristics:—saponification equiv., 217·3; acid value, 22·9; iodine value, 103·9; unsaponifiable matter, 3·1 per cent. (with iodine value, 214·5). The fat was hydrolysed and the liberated acids were steam-distilled until no more acid appeared in the distillate. The non-volatile acids (saponification equiv., 255·6; iodine value, 121·6) were separated into "solid" acids (22·6 per cent.) and "liquid" acids (77·4 per cent.) by the lead salt and alcohol method. The methyl esters of the "solid" and "liquid" acids were then fractionally distilled at 0·1 mm. pressure from a Willstätter bulb, and the individual fractions were examined by the usual methods. From the results it was calculated that the acids consisted of:—formic, 5·8; acetic, 1·8; benzoic, 1·9; palmitic, 19·4; stearic, 3·8; oleic, 14·9; linolic, 37·6; linolenic, 11·7 per cent. The unsaponifiable matter, etc., amounted to 2·95 per cent. To determine whether the acids of low molecular weight were present as glycerides or as other esters, the seed oil (300 g.) was dissolved in petroleum spirit (b.p. 40 to 60° C.) and extracted 20 times with 200-ml. portions of 80 per cent. methyl alcohol, which removed 83 g. of fat; this fraction was re-extracted 5 times with the alcohol. Examination of these fractions indicated that the portions soluble in petroleum spirit were mainly glycerides, and that the portion soluble in methyl alcohol consisted of a mixture of glycerides and esters of a dark syrupy tetrahydroxylic water-soluble alcohol (the acetyl derivative was a transparent, pale yellow resinous solid, with saponification equiv., 110·3). The approximate composition of the alcohol is $C_{15}H_{26}O_5$; its nature has not been definitely ascertained. It was found that the formic, acetic and benzoic acids were present as esters of this compound, and not as the glycerides; they are soluble in the fat and are extracted with it.

Fruit-coat fat.—The acids liberated after hydrolysis were steam-distilled until the distillate was free from acid. They were then treated in the same way as the seed-fat acids, the respective methyl esters being fractionally distilled. From the examination of the fractions it was calculated that the acids had the following composition:—formic, 2·4; acetic, 4·0; benzoic, 2·5; myristic, 2·7; palmitic, 23·8; stearic, 3·7; oleic, 27·8; linolic, 17·4; linolenic, 15·7 per cent.; unsaponifiable matter, 0·19 per cent. The fruit-coat fat was semi-solid and had saponification equiv., 244·8; acid value, 70·1; iodine value, 95·0. It contained 6·6 per cent. of unsaponifiable matter (iodine value, 206·8). An alcohol resembling that of the seed-fat alcohol was isolated. E. B. D.

Seed and Fruit-coat Fats of *Neolitsea involucrata*. B. G. Gunde and T. P. Hilditch. (*J. Chem. Soc.*, 1938, 1610–1614.)—The average composition of fruits of *Neolitsea involucrata*, a Ceylon shrub, similar to, but not identical with, wild cinnamon, which were examined was:—kernel, 64; fruit-coat, 36 per cent. The kernel contained 66 per cent. of dark cream-coloured solid fat, with the following constants:—saponification equiv., 223·3; iodine value, 22·5; acid value, 10·4; unsaponifiable matter, 2·1 per cent. (with iodine value, 175·6). Methyl esters of the mixed fatty acids, with the unsaponifiable matter, were fractionated (*cf.* Longenecker, *J. Soc. Chem. Ind.*, 1937, **56**, 199T) into 9 fractions, and the weight, saponification value and iodine value of each were determined, and the fractions further analysed by methods described in detail. From the results the composition of the fatty acids (freed from unsaponifiable matter) was calculated as:—*n*-decoic, 3·0; lauric, 85·9; myristic, 3·8; oleic, 4·0; linolic, 3·3 per cent. The fat contained 86·7 per cent. of fully-saturated glycerides; by fractionation of the methyl esters of these and analysis of the fractions as before, the composition of the glycerides was calculated to be about 66 per cent. of trilaurin, up to 21 per cent. of dilauromyristin, and possibly a little lauromyristodecoin. The remaining 13 per cent. of the fat consisted of mixed saturated-unsaturated glycerides in which the average "association ratio" of saturated to unsaturated acids was 1·2 to 1. Thus, the glyceride structure of the fat showed the usual maximum formation of mixed, in preference to simple, triglycerides. Owing to the high content of lauric acid in the fat, however, much of this acid remains as trilaurin, even after the other mixed glycerides have been produced.

Fruit-coat fat.—The fruit-coat contained 27 per cent. of an almost liquid fat; it had the following constants:—saponification equiv., 277·5; iodine value, 69·0; acid value, 162·0; unsaponifiable matter, 4·3 per cent. (with iodine value, 111·4). After hydrolysis of the fat and extraction of the unsaponifiable matter from the potassium soaps with ether, the mixed fatty acid were obtained and their lead salts were separated by crystallisation from alcohol into "solid" acids (from the alcohol-insoluble lead salts, 29·4 per cent.) and "liquid" acids (from the alcohol-soluble lead salts, 70·6 per cent.). The methyl esters from each group were fractionated and examined. From the results it was calculated that the component acids had the following composition:—lauric, 10·2; palmitic, 28·2; stearic, 3·1; hexadecenoic, 4·6; oleic, 43·6; linolic, 10·3 per cent.; unsaponifiable matter, 0·27 per cent. The seed-fat of *N. involucrata* forms an excellent source of either lauric acid or trilaurin. E. B. D.

Seed Fat of the Annual Nasturtium (*Tropaeolum var.*). T. P. Hilditch and M. L. Meara. (*J. Chem. Soc.*, 1938, 1608–1610.)—The seeds of the annual garden nasturtium, like those of the tropical perennial, *Tropaeolum majus* (*cf.* Sudborough, Watson, Ayyar and Damle, *J. Indian Inst. Sci.*, 1926, 9, A, 65), contain about 7 to 8 per cent. of fat; the properties and composition of the fat of the seeds of the annual and the perennial plants are similar. The fat is greenish in colour and partly solidifies on keeping, owing to separation of trierucin as a mass of crystalline needles. The constants of the fat from the seeds of self-sown plants (originally "Golden Gleam") were:—saponification equiv., 350·4; iodine value, 75·1; acid value, 4·0; unsaponifiable matter, 1·8 per cent. (yielding a sitosterol, the acetate of which melted at 116° C.). The fat probably contained nearly 40 per cent. of trierucin; this was isolated by crystallisation from alcohol, from benzene, and finally from alcohol at 0° C. Its mp. (31·5 to 32° C.), transition points (vitreous, 5° C.; α-form, 25° C.) and X-ray spectrum agreed with those for synthetic trierucin (Carter, unpublished); the X-ray spectrum was characteristic of trierucin. The mixed methyl esters of the fatty acids were distilled under 0·1 mm. pressure through an electrically heated and packed fractionating column (*cf.* Longenecker, *J. Soc. Chem. Ind.*, 1937, 56, 199T), and from the results the composition of the mixed fatty acids was calculated to be approximately:—palmitic, 0·2; behenic, 0·8; oleic, 16·0; linolic, 1·2; erucic, 81·8 per cent. The seeds are considered to be the most convenient source of erucic acid, owing to its large proportion in the mixed fatty acids and the comparatively simple composition of the remaining acids (mainly oleic), which are readily removed. E. B. D.

Ergot of Rye Oil. H. Vandermeulen. (*J. Pharm. Belg.*, 1939, 21, 195–197, 213–217.)—The oil was a red-brown liquid with a strong green fluorescence. After standing for 3 months at −5 to −10° C. it deposited a small quantity of soft crystals with m.p. 57–60° C. and saponification value, 205; the deposit consisted of a mixture of palmitin and stearin. Two samples of oil were examined, extracted (*a*) with petroleum spirit of low b.p. and (*b*) with light petroleum spirit.

These had the following characteristics:—sp.gr. 15° C., (*a*) 0·9144, (*b*) 0·9237; n_D^{20}, (*a*) 1·4685, (*b*) 1·4696; saponification value, (*a*) 172, (*b*) 182; iodine value (Hanus, 3 hours), (*a*) 62, (*b*) 65; Polenske value, (*a*) 3·14, (*b*) 2; Hehner value, (*a*) 91·5, (*b*) 92; unsaponifiable matter, per cent., (*a*) 3·3, (*b*) 1·3; residue from steam-distillation, (*a*) 0·8, (*b*) 0·9 per cent. Nine kg. of the oil were saponified, and the soluble and insoluble fatty acids and the unsaponifiable matter were separated. The soluble acids were esterified and fractionally distilled; they contained 0·1 per cent. of acetic acid and 0·01 per cent. of caproic acid. The insoluble acids had m.p., 36–40° C.; solidif.p., 32–38° C.; n_D^{40}, 1·4540; iodine value (Hanus), 66·3; acetyl value, 79·3; mean molecular equiv., 301. The acids were separated by Twitchell's method. The saturated acids (42 per cent. of the total acids) had m.p., 53–54° C.; solidif.p., 51–50° C.; n_D^{60}, 1·4355; neutralisation value, 198; iodine value (Hanus), 2·9; acetyl value, 0; mean molecular equiv., 276. They consisted of 70 per cent. of palmitic and 30 per cent. of stearic acid. The separated and purified unsaturated acids had solidif.p., below −10° C.; n_D^{20}, 1·466; neutralisation value, 185; iodine value (Hanus), 85·5; acetyl value, 107·2; mean molecular equiv., 302·5. The non-hydroxy acids consisted of oleic and linolic acids. The high acetyl value indicates the presence of a high proportion of a hydroxy acid, which was finally separated by a method based on the solubility of lead oleate and the insolubility of lead ricinoleate in petroleum spirit. The lead salts of the unsaturated acids were prepared in the absence of all solvent except petroleum spirit. The first crystals still contained some solvent, but after three recrystallisations the white crystals (m.p. 95° C.) were free from solvent; they were dissolved in ether, and the solution was acidified with hydrochloric acid, filtered, and dried over anhydrous sodium sulphate. When the solvent was evaporated an almost odourless slightly yellow oily liquid remained. The hydroxy acid was identified as ricinoleic acid. The unsaponifiable matter (about 1 per cent.) was found to contain one or more sitosterols, ergosterol (about 0·5 per cent. of the mixed sterols) and two other sterols; it also contained an essential oil. It was calculated that the fatty acids consisted of 0·1 of acetic, 0·01 of caproic, 30 of palmitic, 12 of stearic, 23 of oleic, and 34 per cent. of ricinoleic, with traces of linolic acid. No alkaloid was detected in the oil. D. G. H.

Identification of Acetaldehyde in the Steam Distillate of the Peel of Citrus Fruits. J. B. Biale and F. T. Weiss. (*J. Amer. Chem. Soc.*, 1939, 61, 635–636.)—Samples of finely-ground peel from 10 oranges, 15 lemons and 6 grapefruits were steam-distilled in an all-glass apparatus. Exact comparisons between the several varieties were not possible owing to variations in maturity, but the aldehyde-content was of the order 0·05 to 0·1 mg.-equivalents per 100 g. of fresh rind. Most of the aldehyde is regarded as produced during the process of respiration and not by breakdown of substances during distillation. To identify the aldehyde, crystalline derivatives were prepared by steam-distilling the peel of 400 oranges and 300 lemons and concentrating the distillate by repeated distillation from a saturated sodium bicarbonate solution into sodium bisulphite; 80 per cent. of the aldehyde then came over in the first 5 per cent. of distillate. The oil was removed by means of activated carbon, and the concentrated bisulphite aldehyde complex was saturated with sodium bicarbonate and distilled into an acid solution of 2,4-dinitrophenylhydrazine or into an alcoholic solution of dimethylcyclohexanedione. The mixed melting-point determinations showed that most of the aldehyde in the first two fractions of orange peel and that of the first fraction of lemon peel was acetaldehyde. D. G. H.

Reaction for Phosphates in Codeine Hydrochloride. T. Potjewijd. (*Pharm. Weekblad,* **1939, 76,** 213.)—The *Codex Medicamentorum Nederlandicus* recommends the silver nitrate reaction for the identification of codeine phosphate, whilst the Dutch Pharmacopoeia specifies the barium nitrate reagent for distinguishing between codeine phosphate and codeine hydrochloride and for detecting the former in the latter. The author, however, has obtained unsatisfactory results when using these tests with mixtures of these codeine salts, and he has therefore made comparative experiments with barium nitrate, magnesia mixture (with and without the addition of ammonia in each instance) and with ammonia alone. The tests were made on 0·02 per cent. solutions of the pure salts and of mixtures containing codeine hydrochloride with 1 and 5 per cent. of codeine phosphate. A definite positive reaction was obtained with the 1 per cent. mixture on adding 3 drops of the barium nitrate solution followed by 3 drops of ammonia; 3 drops each of magnesia mixture and ammonia gave a similar result, but only after standing. It is suggested that the Dutch Pharmacopoeia should be altered so as to specify that no turbidity should result (*a*) on the addition of barium nitrate solution to a 0·02 per cent. solution of the sample (test for sulphates); (*b*) on the further addition of ammonia to the mixed solutions (test for phosphates). J. G.

Assay of Emetine and Bismuth Iodide and of Emetine Hydrochloride. N. Evers and W. Smith. (*Quart. J. Pharm.,* 1938, **11,** 758–762.)—*Assay of emetine with bismuth iodide.*—The B.P. methods for the determination of emetine and bismuth in emetine and bismuth iodide are criticised on two counts. First, the addition of excess of ammonia, prior to extraction of the alkaloid with chloroform, gives a precipitate of bismuth hydroxide, which makes the extraction extremely difficult and wasteful of solvent. Secondly, the extracted alkaloid is difficult to dissolve in 0·1 *N* sulphuric acid without the application of heat, and emetine is very sensitive to heat. The first difficulty has been overcome by forming bismuth citrate, which is soluble in ammonia, and the second by weighing the extracted emetine instead of titrating it. About 0·5 g. of the salt is dissolved in 5 ml. of acetone and 0·5 ml. of conc. hydrochloric acid by gently heating. The solution is transferred with the minimum of acetone to a separating-funnel containing a solution of 5 g. of citric acid in 10 ml. of water. The mixture is made slightly alkaline by the addition of dilute ammonia solution, then diluted with 50 ml. of water, and extracted with chloroform until the aqueous solution no longer gives a positive test with Mayer's reagent. Each chloroform extract is washed with the same 10 ml. of water in a second separating funnel. The chloroform solution is transferred to a tared flask and the solvent is removed. Two ml. of alcohol are added and evaporated off, and the residue is dried at 100° C. and weighed. The bismuth is determined on a separate 0·5-g. portion. This is dissolved in 50 ml. of dilute nitric acid, and the solution is boiled until no more iodine is evolved. A strong solution of ammonia is added until a slight permanent precipitate is formed. This is removed by the addition of 1 ml. of nitric acid, the solution is heated to boiling, and 30 ml. of 10 per cent. ammonium phosphate solution are added slowly from a burette, the solution being stirred during the addition. The mixture is diluted to 400 ml. with boiling water and, after standing for 1 hour, is filtered through a tared Gooch crucible, and the precipitate is washed with hot 3 per cent. ammonium nitrate solution made just acid with nitric acid. It is then dried and gently ignited and weighed as $BiPO_4$. Iodine is determined by Volhard's method.

The results obtained by the foregoing methods on four samples from different manufacturers were as follows:

Sample	Emetine Per cent.	Bismuth Per cent.	Iodine Per cent.	Moisture Per cent.	Total Per cent.
A	30·15	19·82	48·3	1·4	99·67
B	37·15	12·80	44·1	5·23	99·28
C	30·0	22·93	45·5	1·1	99·53
D	36·4	14·53	42·6	2·95	96·48

Sample D gave reactions for potassium.

Assay of emetine hydrochloride B.P.—About 0·5 g. is dissolved in 50 ml. of water, 10 ml. of 20 per cent. sodium hydroxide solution are added, and the solution is exhaustively extracted with chloroform. The chloroform extracts are washed in succession with the same two 10-ml. portions of water, and then evaporated in a tared flask. Two ml. of alcohol are added and evaporated, and the residue is dried at 100° C. and weighed. This gives the amount of emetine present. The aqueous solution is acidified with dilute hydrochloric acid and made just alkaline with ammonia and re-extracted as before with chloroform. The weight of the residue gives the amount of cephaeline present. That the assay by weight is more accurate than the assay by titration is shown in the following table, which gives the results obtained on three samples from different manufacturers:

Sample	Total alkaloids as emetine by titration Per cent.	Emetine by weight Per cent.	Cephaeline by weight Per cent.	HCl Per cent.	Moisture Per cent.	*p*H of 2 per cent. solution	$[\alpha]_D$*
A	70·5	72·9	0·5	10·99	15·0	5·6	—
B	69·7	72·65	0·39	10·76	16·29	5·6	+12·5°
C	67·3	68·56	0·17	10·23	20·67	5·9	+11·25°

* Two per cent. w/v aqueous solution of the anhydrous salt.

F. A. R.

Iodine Reaction for Caffeine in Tea and Coffee Infusions. H. Valentin. (*Z. Unters. Lebensm.*, 1939, **77**, 248.)—During an investigation of tea and coffee infusions by chromatographic adsorption analysis (Valentin, *Pharm.-Ztg.*, 1937, 527; *Pharm. Zentralh.*, 1938, 409) it was found that Wagner's reagent (a solution of iodine in potassium iodide solution) containing dilute sulphuric acid is an excellent precipitant for caffeine in tea or coffee infusions, the caffeine tetraiodide being precipitated as a dark brown compound insoluble in mineral acids (*cf.* Gomberg, *J. Amer. Chem. Soc.*, 1896, **18**, 331; Abst., ANALYST, 1896, **21**, 193). The infusion (2 ml.) is mixed with 2 ml. of water and 2 ml. of the reagent, which consists of equal parts of dilute sulphuric acid (1 + 5) and approximately *N*/10 iodine solution. Coffee infusions, containing usually about 80 mg. of caffeine per cup, give a stronger reaction than tea infusions, which contain about 50 mg. per cup. An infusion of coffee berries (containing about 2 or 3 mg. of caffeine per cup) gives only a faint turbidity. Infusions of malted coffee, owing to the presence of starch, give a dirty bluish-green precipitate. The reaction is not affected by any substance ordinarily added to tea or coffee, but it is preferable to avoid the addition of milk or cream unless comparison solutions are used. The possibility of a quantitative application of the test according to the procedure of Wallrabe (*Apoth.-Ztg.*, 1931, **21**, 341) was investigated. It is not conveniently applicable to coffee infusions owing to the tedious preliminary separation of chlorogenic acid, which absorbs iodine. It is possible to determine the caffeine in tea infusions by this method if the alkaloid is first separated from other substances by a chromatographic adsorption method.

A. O. J.

Action on Sucrose of the Juice Expressed from Tobacco Stem. A. Wenusch. (*Z. Unters. Lebensm.*, 1939, **77**, 281–283.)—The juice expressed from tobacco stems has the property of causing the gelatinisation of sucrose solutions. By treating 80 ml. of 10 per cent. sucrose solution with 20 ml. of the filtered juice from tobacco plants the following facts were established: Juice from tobacco leaves does not cause gelatinisation in the same time as juice from the stem. Although sucrose solutions gelatinise easily, fructose and glucose solutions treated with tobacco-stem juice under the same conditions remained liquid for several days. The gelatinising action of the juice is stronger if it is collected before the plant has flowered. The rapidity of gelatinisation varies with the species of the plant. Of the three species examined, the juice of *Nicotiana rustica* caused gelatinisation first, the juice of *N. tabacum* next, whilst the juice of *N. macrophylla* had not caused gelatinisation in 8 days. Other conditions being unaltered, the juice acted the more rapidly the higher the concentration of sugar. When the gelatinised sugar solution is thinly spread on a glass plate and allowed to dry at room temperature, a transparent, extraordinarily firm, adhesive film is formed. When treated with water the film swells but is not soluble even in boiling water. Owing to the lateness of the season and the consequent lack of material, further investigation was postponed until the summer of this year. A. O. J.

Biochemical

Storage of Iron in the Organism with Different Iron Preparations. P. Vosskühler. (*Z. physiol. Chem.*, 1939, **257**, 217–231.)—The amount of iron present in various tissues as a result of feeding definite amounts to rabbits for 8, 16 and 28 days, was determined by a micro-histochemical method. Of the five preparations tested, two—ferrum carbonicum saccharatum and "Ferrostabil" (Schering-Kahlbaum)—contained the iron in the ferrous condition, another two—ferrum oxydatum saccharatum and "Blutan" (Helfenberg)—in the ferric condition, whilst the fifth preparation, ferrum reductum, is supposed to be converted into ferrous salt by the action of the acid of the stomach. The rabbits were given a basal diet consisting of carrots, and the iron preparations were given orally in an amount corresponding with 0·1 g. of iron per kg. of body-weight per day—a figure greatly in excess of the physiological requirement. The iron-contents of various tissues and organs were estimated in tissue-slices by means of the Prussian blue and Turnbull's blue reactions. Both methods gave substantially the same results, and it was impossible to distinguish between ferrous and ferric iron in the tissues. Sections of the stomach were made at four points between the cardia and the pylorus, and sections of the small intestine, the vermiform process and the colon at several points also. The amount of iron found to be present in the various organs at the end of 8, 16 and 28 days for each of the iron preparations is summarised in the following table:

PREPARATION

	Ferrum reductum			Ferrum oxydatum saccharatum			Ferrum carbonicum saccharatum		
No. of days ..	8	16	28	8	16	28	8	16	28
Stomach (pre-pyloric) ..	+	+	+	(+)	(+)	(+)	(+)	(+)	+
Duodenum ..	(+)	+	+	(+)	(+)	(+)	+	+	(+)
Small intestine (upper) ..	(+)	+	+	(+)	+	+	(+)	+	++
Colon (upper) ..	+	+	+	+	+(+)	+	+	+(+)	++
Vermiform process	+	+	+	+	+(+)	+	+	+(+)	++
Liver	+	++(+)	+++	+	+(+)	+(+)	+	++	+++
Spleen	+	++(+)	+++	+(+)	+++	++	+++	+++	+++
Kidney ..	—	+	+	—	—	(+)	(+)	+	+(+)
Bone-marrow ..	(+)	+	+	(+)	+	(+)	—	+(+)	+

PREPARATION—*continued*

	"Ferrostabil"			"Blutan"		
No. of days	8	16	28	8	16	28
Stomach (pre-pyloric) ..	(+)	(+)	+	(+)	(+)	(+)
Duodenum	+	+(+)	+	(+)	+	+
Small intestine (upper) ..	—	+	+	(+)	+	+
Colon (upper)	+	++	+	+	+	+
Vermiform process	(+)	+	+	+	+	++
Liver	+	++	++	+	+(+)	++
Spleen	+++	++	+++	++	++	+++
Kidney	(+)	(+)	+	—	(+)	+
Bone-marrow	+	+	+	+	+	+

— = none; (+) = trace; + = small amount; ++ = large amount; +++ = very large amount.

In general, the amount of iron near the pylorus was greater than elsewhere in the stomach, and the amount in the upper portions of both the small intestine and the colon greater than in the lower portions. Similarly, the amount present at the proximal end of the vermiform process was greater than at the distal end. Only after 28 days' feeding did the distribution of iron throughout the gastro-intestinal canal become anything like uniform. There was little difference, if any, in the effect of preparations containing ferrous iron and those containing ferric iron, but the experiments threw no light on the relative efficiency of absorption of ferrous and ferric iron from the storage depots. F. A. R.

Determination of Small Amounts of Pentoses, especially in Derivatives of Adenylic Acid. W. Mejbaum. (*Z. physiol. Chem.*, 1939, **258**, 117–120.)—It has been found possible to determine amounts of pentose from 1 to 25γ by means of Bial's reaction suitably modified. The reagent is made by adding conc. ferric chloride solution to conc. hydrochloric acid until the solution contains 0·1 per cent. of ferric chloride (this solution must be stored in glass-stoppered bottles) and adding 10 mg. of orcinol per ml. immediately before each determination; this solution does not keep. Exactly 0·5 ml. of the solution to be tested is measured into a small tube graduated at 2, 4 and 6 ml., and 0·5 ml. of the reagent is added. The mixture is then immersed in boiling water for 20 minutes, the green solution is diluted to 2 ml. and transferred to the 5-cm. micro-cell of a Pulfrich photometer, and the colour is measured, filter S61 being used. These proportions are for quantities of pentose of 1 to 3γ; for larger amounts, the solution must be further diluted or a 1-cm. cell may be used. The extinction value is strictly proportional to the amount of pentose, whether free or combined, when the quantity present is between 1 and 18γ, and for 2γ in 1 ml. of solution in a 1-cm. cell, it is 0·0536. The value decreases for amounts of pentose in excess of 18γ. The method has been found satisfactory for arabinose, for the barium salt of inosic acid and for muscle adenylic acid. F. A. R.

Determination of Iodine in Biological Materials. C. D. Stevens. (*J. Lab. Clin. Med.*, 1937, **22**, 1074.)—The following simplification of the Trevorrow and Fashena modification of Leipert's method (*cf. J. Biol. Chem.*, 1935, **110**, 29; Abst., ANALYST, 1935, **60**, 628) effects a saving of time, reagents and apparatus. *Reagents.*—(*a*) Iodine-free water, used for all aqueous solutions, is distilled from potassium hydroxide solution; (*b*) 3 per cent. sulphuric acid: 50 ml. of conc. sulphuric acid are boiled for 30 minutes with 2 drops of 30 per cent. hydrogen peroxide and diluted; (*c*) a 5 per cent. solution of anhydrous ceric sulphate in 3 per cent. sulphuric acid; (*d*) chromic acid solution: 250 g. of the acid in 150 ml. of water; (*e*) carborundum pieces are boiled successively in dilute nitric acid and phosphorous acid (10 minutes in each), rinsed, boiled several times in iodine-free water, and heated to redness for 5 minutes; (*f*) potassium oxalate, re-crystallised after precipitation with alcohol from a saturated solution. Bromine should be tested for iodine and potassium iodide must be free from iodate. *Methods.*—The special all-glass apparatus (Fig. 1) consists of a 500-ml. special distillation flask, 10-ml. funnel, and connecting-arm with trap and a condenser (Fig. 2). Ten ml. of blood in the flask are diluted with 10 ml. of water and a piece of carborundum (*e*) is added. Then 17 ml. of chromic acid solution (*d*) are introduced and followed, quickly but cautiously, by 100 ml. of conc. sulphuric acid, the flask being cooled in water and the acid being added in small portions at first and then more rapidly, with shaking after each addition. One ml. of ceric sulphate solution is added, and the flask is heated until bubbling has almost ceased and until, on addition of a few ml. of water, white fumes fill the flask. (With over-heating—usually above 210° C.—bumping occurs and chromous sulphate is precipitated). One hundred ml. of water are then poured slowly on to the mixture and, when bubbling has ceased, the whole apparatus is assembled. Six ml. of a 50 per cent. solution of phosphorous acid are carefully run into the flask, and the funnel is rinsed with 30 ml. of water; the tap is then closed. The mixture is first heated gently to the boiling-point and then distilled rapidly into a 100-ml. Pyrex flask containing 1 ml. of *M* potassium hydroxide solution until, after about 100 ml. have distilled in about 30 minutes, white fumes appear in the condenser. The distillate is kept at a volume of about 5 ml. by boiling it off as it is collected. After disconnection of the apparatus the condenser and receiver are rinsed out (final volume of distillate 15 to 20 ml.), and the solution is titrated drop by drop with 3 per cent. sulphuric acid to a clear pink (not orange-pink) colour, one drop of a 0·02 per cent. solution of methyl orange being used as indicator. In another room, bromine vapour is poured upon the solution, which becomes light yellow on stirring, the excess of bromine is boiled off, and the solution is concentrated to about 2 or 3 ml. and cooled for 5 minutes in a refrigerator to about 10° C. Four drops of 1 per cent. potassium iodide solution and 1 drop of a 1 per cent. solution of starch are added, the sides of the flask are wetted with the solution, and the iodine is titrated with 0·0005 *N* sodium thiosulphate solution, which is delivered in 0·005-ml. portions from a 0·2-ml. graduated serum pipette which is immersed in the solution being titrated. The iodine may be determined in 2 hours with no greater error than in the best micro-methods. No correction is required. For the analysis of urine, samples containing a suitable quantity of iodine are taken, and, if large, are mixed with 1 ml. of saturated potassium hydroxide solution in the digestion flask and evaporated to about 10 ml. The inside of the neck of the flask is rinsed down with 10 ml. of iodine-free water, and the procedure used for blood is followed. Faeces are dried, and 1 g. or 0·5 g. samples are analysed. In test experiments with potassium iodide, potassium iodate and beef blood containing known quantities of iodine (0·81, 0·48, 1·35 and 4·59γ), the amounts found showed the following ranges:—0·64 to 0·79γ; 0·29 to 0·45γ; 1·30 to 1·40γ; 4·58 to 4·68γ. A table is given showing the amounts of iodine in the blood of persons suffering from various disorders and known to have had iodine treatment within 9 days before the sample was taken. E. B. D.

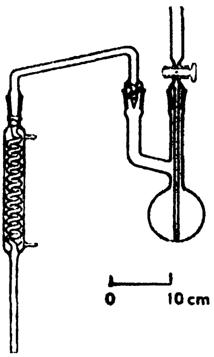


Fig. 1

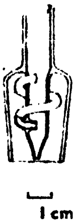


Fig. 2

Iodine in Pituitary and some other Tissues. E. J. Baumann and N. Metzger. (*J. Biol. Chem.*, **1939**, **127**, 111–115.)—The hypothesis, that in thyroid deficiency the anterior lobe of the pituitary gland can act for the thyroid, was tested by determining the amount of iodine present in the hypophysis of human beings and various animals, since many earlier workers claimed to have found appreciable amounts of iodine there. Most of the analyses were made by the method previously described (*cf.* ANALYST, **1937**, **62**, 887), which will detect 0·1γ of iodine with certainty. No iodine, however, was found to be present in hypophyses of human beings who had not received iodine medication, though up to 150γ per 100 g. were found in subjects that had been given iodine for some time before death. From the analyses made of the iodine-contents of the hypophysis, ovary, testis, kidney, spleen and blood, of various animals, it would seem that the hypophysis normally contains no more iodine than these other organs.

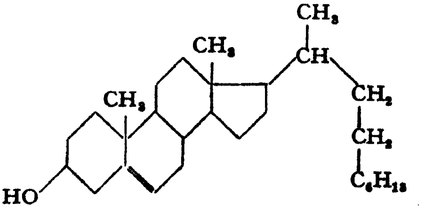
F. A. R.

Determination of Cholesterol. F. E. Kelsey. (*J. Biol. Chem.*, **1939**, **127**, 15–22.)—The use of the Liebermann–Burchard colour reaction for the determination of cholesterol in blood lipids without saponification leads to results 10 to 20 per cent. higher than those obtained by precipitation with digitonin, and, moreover, is sometimes affected by other colours in, or produced by, the blood extracts. A method that gives reasonably accurate results is obtained by combining precipitation by digitonin with the Liebermann–Burchard reaction. An alcohol-ether extract of the blood or tissue is made according to the method of Bloor (*J. Biol. Chem.*, 1929, **82**, 273), an aliquot portion of the solution, containing about 0·5 mg. of cholesterol, is evaporated to dryness, and the residue is treated with a mixture of 10 ml. of 1 : 1 alcohol-ether and 0·3 ml. of 30 per cent. potassium hydroxide solution. The mixture is allowed to stand in a warm place for half-an-hour to hydrolyse the cholesterol esters, and is then treated with sufficient dilute hydrochloric acid to neutralise the alkali previously added. The solution is next extracted several times with petroleum spirit, and the combined extracts are concentrated to 0·5 ml. in a 15-ml. centrifuge tube. To this solution are added 4·0 ml. of a 0·2 per cent. solution of digitonin in 95 per cent. alcohol, the mixture is evaporated to dryness, and contaminating substances are dissolved out by boiling the precipitate with 12 ml. of petroleum spirit. The tube is centrifuged for 3 to 4 minutes, and the supernatant liquid is decanted and discarded. The extraction is repeated twice, and the final residue is gently boiled with 7·0 ml. of benzene for 45 minutes to decompose the digitonide, benzene being added occasionally to replace that lost by evaporation. The contents of the tube are finally concentrated to 3 ml. and diluted to 12 ml. with petroleum spirit. Digitonin separates on stirring and is centrifuged off. The supernatant liquid is decanted, and the residue is re-extracted three times with petroleum spirit. The combined extracts are evaporated to dryness, the residue is dissolved in exactly 5·0 ml. of chloroform, and the solution is transferred to a 10-ml. glass-stoppered graduated cylinder. Five ml. of a chloroform solution of 0·5 mg. of cholesterol are measured into another cylinder, and 1·0 ml. of acetic anhydride and 0·1 ml. of conc. sulphuric acid are added to each. After being well mixed, the solutions are maintained at about 23° C. for

15 minutes, and the colours that develop are compared in a colorimeter. The amount of free cholesterol was determined in a similar manner after precipitation of phospholipids according to the method of Bloor (*loc. cit.*), and the acetone-soluble fraction was concentrated to 0·5 ml. The results obtained with solutions containing known amounts of cholesterol palmitate and cholesterol were 98·5 per cent. of the calculated value for total cholesterol and 101·9 per cent. for free cholesterol. Cholesterol added to an alcohol-ether extract of plasma was determined, with a percentage error of 4·6 for the total sterol and 1·5 for the free sterol.

F. A. R.

Comparison of Cinchol with Sitosterol and Stigmasterol. W. Dirscherl. (*Z. physiol. Chem.*, 1939, **257**, 239–245.)—Previous work on cinchol, the sterol of cinchona bark, had suggested that it was identical with sitosterol and 22 : 23-dihydrostigmasterol, but it has since been shown that "sitosterol" itself is a mixture of four sterols, now termed α_1-, α_2-, β- and γ-sitosterol. A careful comparison has therefore been made of cinchol, β- and γ-sitosterol and 22 : 23-dihydrostigmasterol and many of their derivatives. This shows that cinchol, β-sitosterol and 22 : 23-dihydrostigmasterol are very probably identical with one another but different from γ-sitosterol. There exists the possibility, however, that cinchol differs from 22 : 23-dihydrostigmasterol in the structure of the group C_6H_{13} in the side-chain. The following formula is provisionally assigned to cinchol:



F. A. R.

Chemical Reagent for Thiamine (Aneurin). H. J. Prebluda and E. V. McCollum. (*J. Biol. Chem.*, 1939, **127**, 495–503.)—Solutions of aneurin give purple-red precipitates with solutions of the alkaline diazotates of *p*-aminoacetanilide and *p*-aminoacetophenone, and the reaction was found to be so specific that it is proposed as a method of detecting and estimating the vitamin, the latter reagent being preferred for the purpose. The solutions required are as follows:—*Solution A.*—3·18 g. of *p*-aminoacetophenone are dissolved in 45 ml. of conc. hydrochloric acid and the solution is made up to 500 ml. with water. This solution, if stored in the dark, will keep for 6 months. *Solution B.*—22·5 g. of sodium nitrite are dissolved in water and the solution is made up to 500 ml. *Solution C.*—20 g. of sodium hydroxide are dissolved in 600 ml. of water, and 28·8 g. of sodium bicarbonate are added to the solution, which is then made up to 1 litre. *Diazo Solution.*—One volume of Solution A is added to 1 volume of Solution B, both solutions being first cooled to 0° C. After 10 minutes' stirring, a further 4 volumes of Solution B are added, and the mixture is stirred at 0° to 5° C. for 20 minutes. When 20 ml. of this solution (which keeps for about 12 hours at 0° C.) are added to 275 ml. of Solution C, a purple colour, which disappears on stirring for 5 to 10 minutes, is formed. The solution is adjusted to *p*H 5 to 6.

Reaction with aneurin.—On the addition of 2 ml. of the reagent to 1 ml. of aneurin solution, a purple-red colour develops within 20 minutes, and when the mixture is allowed to stand, a precipitate of the same colour is deposited. This precipitate can be extracted with isobutyl alcohol, toluene or xylene, as well as with other solvents, to give coloured solutions. The colour of these solutions obeys Beer's law. Of 46 substances of biological importance that were tested with the diazo reagent, only one, inositol, gave a coloured precipitate, but this was insoluble in aromatic solvents. Thiazoles gave a reaction similar to that obtained with aneurin. F. A. R.

Chemical Determination of Vitamin B_1. I. Reaction between Thiamine in Pure Aqueous Solution and Diazotised *p*-Aminoacetophenone. D. Melnick and H. Field. (*J. Biol. Chem.*, 1939, 127, 505–514.)—The use of diazotised *p*-aminoacetophenone for determining aneurin was investigated, the reagent being used exactly as described by Prebluda and McCollum (*cf.* preceding abstract). The precipitate was best extracted from the aqueous suspension by means of xylene. When 10 ml. of vitamin solution and 20 ml. of the reagent were used it was found that the reaction was complete after standing for 15 hours (overnight), and that, in order to avoid destruction of aneurin, its solution must be made just alkaline to litmus and the reagent added immediately. The vitamin could then be estimated with an average error of about ± 2 per cent., the limit of the test being reached with 5γ per ml. F. A. R.

Chemical Determination of Vitamin B_1. II. Method for Estimation of the Thiamine Content of Biological Materials with the Diazotised *p*-Aminoacetophenone Reagent. D. Melnick and H. Field. (*J. Biol. Chem.*, 1939, 127, 515–530.)—In attempting to apply the diazotised *p*-aminoacetophenone reagent (*cf.* preceding abstracts) to the determination of aneurin in biological material, it was found that impurities that inhibited the reaction were often present. One way of overcoming the inhibition was to add to the vitamin solution phenol or alcohol, or better still a mixture of the two; the presence of these substances apparently neutralised the effect of the inhibitor and at the same time increased the sensitivity of the reaction, minimised errors due to deviation from standard conditions, and exerted an appreciable protective effect on the vitamin in solutions alkaline to litmus. In addition, however, it was found essential to purify the vitamin solution very considerably before applying the colour reaction, and the essential step in this purification was adsorption on permutit followed by elution with hot acidified potassium chloride solution. In the analysis of rice polishings, wheat germ and yeast, which contain only small amounts of salts, sufficient of the powdered material to yield an extract containing 150γ of aneurin was extracted by stirring with 20 to 30 parts of water at 70° C. for 30 minutes, the *p*H of the suspension being adjusted to 4·5 and the air replaced by nitrogen. The suspension was centrifuged and the extract and washings were treated with permutit, as described below. Alternatively, the extraction can be carried out with 80 per cent. methyl alcohol, but the alcohol must be distilled off from the extract prior to adsorption. In analysing a liver extract, the procedure described above cannot be followed, as the presence of salts in the liver interferes with the adsorption. The most efficient recovery of vitamin was obtained by dissolving the liver extract in the smallest possible amount of water and, after saturating the solution with sodium sulphate, concentrating under reduced pressure to a syrup. Benzyl alcohol was then added, and the concentration was continued until no aqueous phase remained. Aneurin was recovered from the benzyl alcohol extract so obtained by adding acidified water of *p*H 3 to 4 and an excess of ether (5 volumes). The aqueous phase was distilled under reduced pressure to remove dissolved ether and could then be treated with permutit. This procedure also appears to be applicable to the analysis of urine.

The adsorption of aneurin on permutit was carried out as follows: A large batch of permutit was freed from alkali by the method of Cerecedo and Kaszuba (*J. Amer. Chem. Soc.*, **1937**, **59**, **1617**), and then washed 5 times with distilled water, 3 times with 95 per cent. ethyl alcohol, once with acetone and finally twice with anhydrous ether, and dried and stored for future use. Exactly 3 g. of the purified adsorbent were poured into a "filter-tube," 8 mm. in diameter, having a plug of glass-wool at the lower end. This filter-tube was inserted into the neck of a filter-flask by means of a rubber stopper, and to its top end was attached a condenser through the jacket of which steam could be passed. The top of the condenser was closed with a rubber stopper, carrying a tube attached to a nitrogen cylinder and another tube connected with the vessel containing the aneurin solution. When fresh permutit was used, it was first washed in the filter-tube by running in 30 ml. of 25 per cent. potassium chloride solution acidified to *p*H 2 and heated by being retained in the steam-jacketed tube for a few minutes. This solution was followed by 500 ml. of hot distilled water. The flow of steam through the jacket was then stopped, and the apparatus was filled with nitrogen. The vitamin solution at *p*H 4·5 was then allowed to syphon over into the filter-tube and run slowly by gravity through the permutit. It was followed by 30 ml. of wash-water at *p*H 4·5, heated by being retained in the steam-jacketed tube; this wash-water was run rapidly through the permutit, and was followed by acidulated potassium chloride solution, similarly heated. This solution, which eluted the vitamin, was run slowly through the permutit and the eluate was collected in a tube, graduated at 10 ml., which was attached to the bottom of the filter-tube (inside the filter-flask) by means of hooks placed there for that purpose. The permutit was washed with 500 ml. of hot, distilled water and was then ready for another analysis. The eluate was made up to 10 ml. and 3 ml. were pipetted into a 50-ml. centrifuge bottle and mixed with 3 ml. of 95 per cent. alcohol solution containing 5 mg. of phenol per ml. After addition of a drop of thymol blue indicator *N* sodium hydroxide solution was added dropwise until a faint but positive blue colour appeared. A fine stream of nitrogen was bubbled through the solution in the meantime. Six ml. of the Prebluda–McCollum reagent were added, and the bottle was stoppered and allowed to stand overnight at room temperature. The solution was then shaken vigorously for 1½ minutes with 2 ml. of xylene, and the two layers were separated by centrifuging. The colour of the xylene solution was compared in a microcolorimeter with the colour of a standard solution similarly prepared. The colour of the indicator and colours produced by impurities are not extracted by xylene. It is recommended that a series of tests be carried out with the same permutit filter; one blank will then serve for all. No calibration curve is necessary, as the intensity of the colour in the xylene layer varies directly as the concentration of aneurin. Recoveries of 94 to 104 per cent. of the aneurin present in pure solutions and of 96 to 105 per cent. of the aneurin added to various kinds of biological material were obtained. By this method, only free aneurin is determined, and not aneurin present in the phosphorylated state. F. A. R.

Chemical Determination of Vitamin B_1. III. Quantitative Enzymic Conversion of Co-carboxylase (Thiamine Pyrophosphate) into the Free Vitamin. D. Melnick and H. Field. (*J. Biol. Chem.*, 1939, **127**, 531–540.)—It is not possible to determine phosphorylated aneurin by reaction with diazotised *p*-aminoacetophenone until it is hydrolysed to the free vitamin. This has been accomplished with the aid of a hot air-dried yeast powder which contains an enzyme apparently liberated on drying. The optimal conditions for enzymic hydrolysis were a *p*H of 4·5, a temperature of 45° C. and incubation for 12 hours. The activity was found to be associated with a water-soluble protein fraction of the yeast powder. Biological material of various kinds was treated with the yeast phosphatase, and the total aneurin was determined by causing the hydrolysate to react with diazotised *p*-aminoacetophenone. Free aneurin was determined on a sample prior to hydrolysis, and phosphorylated aneurin was calculated by difference. The results for the total aneurin determined chemically and biologically agreed well. F. A. R.

Isolation and Detection of α-Carotene, and the Carotenes of Carrot Roots and of Butter. H. H. Strain. (*J. Biol. Chem.*, 1939, **127**, 191–201.)—The carotenoid pigments of carrots and of butter were studied with the aid of chromatographic adsorption and absorption spectroscopy. It was found possible to separate α- and β-carotenes without destroying either, by using magnesia as the adsorbent. When a petroleum spirit extract of carrots was hydrolysed and the epiphasic fraction of the carotenoids so obtained was chromatographed, zones corresponding to the following compounds were formed (from the top of the column downwards): γ-carotene, δ-carotene, a flavoxanthin-like carotenoid not yet characterised, β-carotene, α-carotene, colourless fluorescent substances similar to those found in carrot leaves, and an unknown carotenoid. The butter made from the milk of cows fed on different diets was then examined by the same technique. It was found that when the rations contained β-carotene as the principal carotenoid, the butter carotene consisted almost entirely of β-carotene, and that when substances were fed that were rich in α-carotene, the flavoxanthin-like pigment and the fluorescent substances, these compounds made their appearance in the butter in proportion to the amounts present in the rations. It seems evident, therefore, that the carotenoid-content of butter is largely conditioned by the rations that the cows receive. F. A. R.

Improved Method for Estimating Carotene in Feeds. G. S. Fraps and A. R. Kemmerer. (*J. Assoc. Off. Agric. Chem.*, 1939, **22**, 190–194.)—For the selective adsorption method of determining carotene it is essential to use as adsorbents magnesium hydroxide preparations which adsorb xanthophyll completely but do not adsorb carotene. *Testing the magnesium hydroxide.*—Fifty g. of suitable (U.S.P. light) magnesium oxide are heated with 50 ml. of water for 30 minutes in an evaporating dish on the water-bath. Half-a-gram of this activated material is shaken with 10 ml. of purified carotene solution (or 2·5 g. with 50 ml.) and the magnesium hydroxide is allowed to settle, or the liquid is centrifuged. The colour is read by the usual method before and after the treatment. The magnesium hydroxide is tested with the xanthophyll solution in the same way. If the magnesium hydroxide adsorbs all the xanthophyll and none of the carotene, it is suitable for use; if it does not, another sample is tested. *Preparation of the carotene solution.*—Pure carotene (0·1 g.) is dissolved in 2 ml. of chloroform and precipitated with about 25 ml. of methanol, and the precipitate is filtered off and dried between filter-paper and in a vacuum desiccator. Twenty mg. of this carotene are dissolved in a few drops of chloroform, and the solution is made up to 50 ml. with light petroleum spirit; 5 ml. are diluted to 1 litre with light petroleum spirit. *Preparation of the xanthophyll solution.*—About 6 g. of alfalfa are "saponified" with 120 ml. of alcoholic potash and extracted with U.S.P. ethyl ether as directed in the published method for carotene (Fraps and Kemmerer, *Texas Agr. Exp. Sta. Bull.*, 1937, No. 557, 1–28). The ether is evaporated and the residue is taken up with light petroleum spirit and washed with 90 per cent. methanol until the washings are colourless. The methanol fraction is then extracted twice with petroleum spirit to remove traces of carotene, the petroleum spirit fraction is extracted with 90 per cent. methanol as directed above, and the methanol extract is added to the original methanol solution. The methanol is evaporated under reduced pressure, the residue is taken up in 100 ml. of petroleum spirit, and the solution is dried over anhydrous sodium sulphate and diluted to contain the equivalent of 2 p.p.m. of carotene. *Determination of the carotene.*—The carotene solution is prepared in the usual way, the colour is read, and the crude carotene is estimated if desired. If necessary, the solution is adjusted to contain about 2 p.p.m. of the colour equivalent to carotene. The solution is shaken with 0·5 g. of magnesium hydroxide per 10 ml. of solution, and the colour is read by the usual method, the result being given as pure carotene in p.p.m. E. M. P.

Isolation of Vitamin K as a Choleic Acid. H. J. Almquist and A. A. Klose. (*J. Amer. Chem. Soc.*, 1939, **61**, 745–746.)—Concentrates prepared by methods already noted (*J. Amer. Chem. Soc.*, 1939, **61**, 532) were dissolved in warm ethanol, and an amount of deoxycholic acid equal to five times the weight of the concentrate was added. The solution was evaporated to dryness at a gentle heat in a current of inert gas, the residue was dissolved in approximately 2 ml. of methanol per 100 mg., and 0·05 ml. of water was added. The mixture was cooled at 0° C. for several hours, and the precipitate was filtered off and dried, and either recrystallised by the same procedure, or, with crude concentrates, water was added to the methanol solution until distinct turbidity was produced, and the first crop of crystals was discarded. Fractional crystallisation was continued by concentrating the solution or by adding more water. From the purest concentrates a vitamin K choleic acid (m.p. 186–187° C.) was obtained repeatedly, and no other fraction except deoxycholic acid itself could be isolated. High vitamin activity was confirmed by restoring normal clotting time to deficient chicks within 24 hours, and from preliminary titrations about 10 per cent. of vitamin K was estimated to be present. The vitamin K choleic acid was a slightly yellow crystalline solid; the vitamin liberated from the acid and freed from traces of solvent and deoxycholic acid reappeared as a viscous slightly coloured oil, bearing no resemblance to the crystalline product (m.p. 60° C.) described by Doisy and co-workers (*Science*, 1938, **88**, 243). D. G. H.

Leprotin, a Carotenoid of the Formula $C_{40}H_{54}$. Y. Takeda and T. Ohta. (*Z. physiol. Chem.*, 1939, **258**, 6–8.)—A red pigment, leprotin, was isolated by Grundmann and Takeda (*Naturw.*, 1937, **25**, 27) from a chromogenic mycobacterium by extracting the dried organisms with acetone. The pigment has now been purified by distributing the saponified extract between petroleum spirit and methyl alcohol, and then chromatographing the petroleum spirit extract on a column of alumina. After two recrystallisations from benzene and methyl alcohol (2:1), the pure pigment had m.p. 198° to 200° C. Its solutions had the following absorption maxima:

Solvent	mμ	mμ	mμ
Carbon disulphide	517	479	447
Chloroform	495	460	428
Petroleum spirit (70°–80° C.)	484	452	425

Leprotin has the formula $C_{40}H_{54}$ and contains 12 double-linkages. It behaves as a provitamin A, for rats with severe xerophthalmia were completely cured by the administration of 20γ per day for 10 days. It is possible that leprotin is a dehydro-β-carotene. F. A. R.

Bacteriological

New Light on the "Sarcina" Question. J. L. Shimwell and W. F. Kirkpatrick. (*J. Inst. Brewing*, 1939, **34**, 135–145.)—Cultures of these organisms have been obtained from various beers in different countries and studied from a comparative point of view. As a result of this study, together with a critical review of the "sarcina literature," the conclusion has been reached that the so-called "beer-sarcinae" or "beer-pediococci" are not sarcinae, "pediococci" or micrococci, but morphologically, culturally and physiologically, belong to the plant division of the genus *Streptococcus*. As a result of the acceptance of this view, the literature on the streptococci has become available for application to beer-stability problems, and arising therefrom, the discovery has been made that the characteristic honey-like odour of "sarcino-sick" beer is due to the production of diacetyl by the beer-cocci. The aroma of fresh butter and that of "sarcina-sick" beer is thus due to the presence of the same substance (diacetyl) produced by organisms of the same type, the well-known "aroma-streptococci." Previous work on the beer-sarcinae is reviewed and summarised, and the summary includes the classification of the genus micrococcus into nineteen species as proposed by Hucker, investigations of the beer-sarcinae by Claussen (1904–06), in which two species were recognised and described, *viz. Pediococcus damnosus* and *P. perniciosus*, and investigations by Mees (1935), who found that the beer-sarcinae were catalase negative and were true lactic acid bacteria, and proposed placing them in a new genus to which the name *Pediococcus* was to be given. In the present investigation a comparative study was made of the "beer-sarcina" including cultures provided by Claussen of *Pediococcus damnosus, perniciosus* and *viscosus* and *Streptococcus lactis, Str. bovis, Str.* (*Leuconostoc*) *mesenteroides, Str.* (*Leuconostoc*) *citrovorus* and *Str.* (*Leuconostoc*) *dextranicus* from the national Collection of Type Cultures. It soon became evident that, apart from the alleged tetrad formation, these organisms exactly corresponded culturally and physiologically, and it was found that chain formation occurred under suitable conditions in all and, moreover, that the streptococci also formed tetrads, both these points being demonstrated by photomicrographs. The *Leuconostoc* species are of commercial importance in dairying, for they produce the characteristic aroma of butter due to the formation of diacetyl. A proof that the honey-odour of "sarcina-sick" beer is due to diacetyl is afforded by distilling such beer and applying the Voges–Proskauer reaction to the distillate. "Sarcina-odour" can, in fact, be given to beer by the addition of minute traces of diacetyl. Hop antiseptic has generally the greatest effect on the Gram-positive bacteria, but among these the streptococci are the most resistant, and with acclimatisation they may acquire enhanced resistance. The optimum *p*H of the strains studied varied, the average being 5·0 to 6·0. Very low figures, however, were obtained in hopped beer; with one strain the *p*H was 3·6, which is even lower than that usually produced by *L. pastorianus*. The impression was gained that the relation to hydrogen ion concentration might be modified by long adaptation to an acid medium. The paper closes with a full description of the characters of the "beer-sarcina" streptococcus, for which the name "*Streptococcus damnosus* (Claussen) Shimwell and Kirkpatrick" is suggested. D. R. W.

Toxicological and Forensic

Effect of Grinding on the Solubility of Mineral Substances and on the Toxic Character of the Resulting Dusts. M. W. Travers. (*Chem. and Ind.*, **1939, 58,** 226.)—A study of the literature of the past few years concerning silicosis has called attention to a few facts apparently unnoticed hitherto but which appear to be of great importance. Although it is known that silicosis results from exposure to an atmosphere containing fine dust, it has been assumed that such dust is only to be produced by mechanical means and that the only effect of the mechanical processes involved is the reduction of the material to powder. In an investigation of the effect of long grinding upon silica sand, Ray (*Proc. Roy. Soc.*, **1923, 102A,** 445) has shown that the effect was to convert a considerable portion of the silica into a state in which its heat of solution in hydrofluoric acid was greater than in the crystalline state, while its density was lowered. It follows that the solubility of the ground silica would be higher than that of crystalline silica, and this may be connected with the poisonous character of mechanically produced dusts. Silicotic lung tissue generally contains microcrystalline material which cannot be identified. This is probably silica in the crystalline state separated from the lung fluids which have been in contact with the mechanically transformed silica and so become supersaturated. The presence of this microcrystalline material has probably no connection with the toxic property of the silica. A. O. J.

Organic

Identification of Olefines as Dithiocyanates. O. C. Dermer and G. A. Dysinger. (*J. Amer. Chem. Soc.*, 1939, **61**, 750.)—Addition of thiocyanogen to a number of common olefines produced two solid dithiocyanates already known and only two new solids—ethylene dithiocyanate, m.p. 90°–90·5° C.; styrene dithiocyanate, m.p. 102·5°–103° C.; cyclohexene dithiocyanate, m.p. 58·0°–58·5° C.; 3-methylcyclohexene-dithiocyanate, m.p. 69·5°–70·0° C. Most of the compounds tested yielded only oily dithiocyanates. The reaction was carried out either by adding the olefine to a suspension of sodium thiocyanate and anhydrous cupric sulphate in glacial acetic acid, or by adding it to a suspension of plumbous thiocyanate in thiophene-free benzene containing bromine. It is considered probable that selenocyanogen would give derivatives of higher m.p., but practical considerations would render this reagent unsuitable. D. G. H.

Identification of Alkyl Phenyl Sulphides, Sulphoxides and Sulphones. V. N. Ipatieff and B. S. Friedman. (*J. Amer. Chem. Soc.*, 1939, **61**, 684–689.)—Alkyl phenyl sulphides cannot be identified by means of mercuric chloride, since co-ordination proceeds very slowly if at all, but with palladous chloride solid derivatives of the type $(C_6H_5{-}S{-}R)_2PdCl_2$ with suitable physical properties are formed in all but a few instances. For these the following methods may be tried: oxidation of the sulphide to sulphone; nitration of the sulphone to form *m*-nitrophenylalkyl sulphone; reduction of the latter to the amino sulphone, or acetylation of the aminosulphone with *m*-bromobenzoyl bromide or *p*-bromobenzoyl chloride. Alkyl phenyl sulphones and sulphoxides may also be identified by means of these reactions, for the sulphoxides can be readily oxidised to sulphones or reduced to sulphides. Aroylation of the amino sulphones in the presence of pyridine is frequently unsuccessful owing to formation of the anhydride derived from the aroyl halide. If dilute alkali is substituted for pyridine, *m*-bromobenzoyl bromide reacts with the amines to form N,N-dibromobenzoyl derivatives, whereas *p*-bromobenzoyl chloride give only N-bromobenzoyl derivatives. Small amounts of *t*-butyl or *t*-amyl phenyl sulphides, in mixtures of each with its isomers, may be detected by means of palladous chloride derivatives, but *t*-butyl and *t*-amyl phenyl sulphones must be nitrated by a special process, as, unlike their isomers, they decompose when nitrated at 100° C. Details are given for the preparation of palladous chloride complexes of alkyl phenyl sulphides, the alkyl phenyl sulphones, the *m*-nitrophenylalkyl sulphones, *m*-aminophenyl sulphones, *m*(di-3-bromobenzoylamino)-phenyl alkyl sulphones, and *m*-(4-bromobenzamino)-phenyl alkyl sulphones; for the use of pyridine in aroylation of *m*-aminophenyl sulphones, *m*- and *p*-bromobenzoic acid anhydrides, and for 3-bromo-4-methyl benzophenone. A table of 43 alkyl derivatives with their properties and elementary composition is also included. D. G. H.

Identification of Polynitro Aromatic Compounds as Addition Compounds with Naphthalene. O. C. Dermer and R. B. Smith. (*J. Amer. Chem. Soc.*, 1939, **61**, 748–750.)—In order to identify polynitro aromatic compounds independently of the reactivity of any special group they may contain, the reverse procedure of that used in identifying condensed ring aromatic compounds has been investigated. Polynitro compounds either commercially available or commonly encountered have been used, and in each instance the polynitro compound-naphthalene system was investigated by an application of cooling-curve technique to the method used by Baril and Hauber (*J. Amer. Chem. Soc.*, **1931**, **53**, 1087) for hydrocarbon picrates. Of the 17 new derivatives tabulated, all but 4 can be recrystallised without decomposition. Twenty-nine polynitro compounds yielded no 1:1 complexes with naphthalene. Although the method of identification is not general in application, it is rapid and simple, and the only possible impurities —the original reagents—present in the derivatives formed may usually be readily removed by recrystallisation. It is difficult to correlate structure of a polynitro compound with its ability to give a stable complex. Although stability is usual, phenolic esters, for example, give unstable complexes, whilst at the other extreme polynitro amines rarely yield compounds with naphthalenes. Results confirm the inhibiting effect of methyl groups situated between nitro groups on the ability of the latter to cause compound formation. At least two nitro groups must be present on each ring if addition compounds are to be formed, but position is of consequence. Thus nitro groups in the ortho position to each other seem to diminish ability to promote reaction. The preponderance of polynitro compounds of high melting-point among those that formed no addition products suggests that the melting-point rather than structure of the polynitro compounds is the dominant factor. D. G. H.

Determination of *p*-Phenylenediamine and *p*-Tolylenediamine. R. L. Herd. (*J. Assoc. Off. Agric. Chem.*, **1939**, **22**, 158–161.)—The method, which is suitable for the determination of *p*-phenylenediamine or *p*-tolylenediamine in hair-dye preparations, in which starch, sulphur, and sulphites may be present, is as follows:—One g. of the sample is dissolved in water in a 200-ml. flask and the flask is filled up to the mark. An aliquot portion of this solution containing 0·06 to 0·08 g. (a smaller quantity may be used) is transferred, with thorough mixing during the addition, to a separating funnel containing 5 ml. of 5 per cent. aqueous sodium hypochlorite solution. Insufficient sodium hypochlorite is indicated by a brown colour while the solution is being added. The funnel is stoppered and shaken for about 10 seconds, after which 10 ml. of 10 per cent. disodium hydrogen arsenite solution are added, and the funnel is stoppered again and shaken. The benzoquinonedichlorimide is extracted with two portions of 25 ml. of chloroform, and the extracts are united in a second separating funnel, washed with 10 ml. of water, and filtered through a plug of cotton-wool into an iodine flask. An additional extraction is carried out, and the extract is washed with water and added to the major portion. Fifty ml. of water containing 1 g. of potassium iodide and 3 ml. of hydrochloric acid are added to the combined extracts, and the funnel is stoppered and shaken vigorously for 1 minute. The liberated iodine is titrated with 0·1 N sodium thiosulphate solution, the flask being stoppered and shaken vigorously at intervals during the titration, and starch solution is added for the final end-point. One ml. of 0·1 N sodium thiosulphate solution is equivalent to 0·001801 g. of *p*-phenylenediamine or 0·002035 g. of *p*-tolylenediamine.

The quinonedichlorimide may be used as an aid in establishing the identity of the *p*-diamine, the procedure being as follows:—Sufficient material to represent about 0·5 g. of the diamine is dissolved in 10 ml. of water, and the solution is transferred to a separating funnel and extracted with 2 portions of 25 ml. of petroleum spirit. The aqueous layer is transferred to a second separating funnel containing 25 ml. of sodium hypochlorite solution, as directed above. The dichlorimide is extracted with about 10 ml. of petroleum spirit and the petroleum spirit layer is washed with about 10 ml. of water. The extract is filtered through cotton into a 50-ml. beaker. The petroleum spirit is evaporated with gentle heat and the residue is dried in a vacuum desiccator. About 0·1 g. of the dichlorimide is weighed out accurately and titrated as in the directions above. The molecular weight of the dichlorimide is calculated from the number of ml. of 0·1 *N* sodium thiosulphate solution used, and compared with the theoretical.

$$\text{Molecular weight} = \frac{60{,}000 \times \text{weight of sample}}{\text{ml. of sodium thiosulphate}}$$

E. M. P.

Inorganic

New Method of Determining Cadmium. **C. I. Nikitina.** (*Zav. Lab.*, 1938, **7**, 409–412.)—The formation of a double salt of cadmium bromide and brucine (*cf.* Meurice, *Ann. Chim. anal. appl.*, 1926, **2**, 130, Abst., ANALYST, 1926, **51**, 367 and Korenman, *Zav. Lab.*, 1937, **6**, 1461, Abst., ANALYST, 1938, **63**, 454) is the basis of a quantitative method for the determination of small amounts of cadmium in presence of much larger amounts of magnesium, aluminium, copper, manganese or zinc. The method, which is very simple, convenient and rapid, is as accurate as the hydrogen sulphide and sulphuric acid method. It has been adapted to the determination of cadmium in magnesium alloys, as follows:—The alloy is dissolved in 10 to 15 ml. of sulphuric acid (1: 5), the solution is evaporated to 5 to 8 ml., and silica, if present, is filtered off. To the neutralised solution, if less than 5 mg. of cadmium are present, are added 5 ml. of a 1 per cent. solution of brucine in sulphuric acid (1: 5) and immediately afterwards 10 ml. of 10 per cent. potassium bromide solution, and the liquid is thoroughly stirred until precipitation is complete. After standing for 1 hour, the precipitate is collected on a sintered glass crucible and washed 5 or 6 times with a mixture containing 40 ml. of 1 per cent. brucine sulphate solution, 30 ml. of 10 per cent. potassium bromide solution and 80 ml. of water, 3 to 5 ml. of this being used each time. The precipitate is then washed 8 or 10 times with an alcohol-ether (1: 7) mixture (portions of 3 ml. being used and the walls of the crucible washed down each time), dried for 30 minutes at 130 to 150° C. and weighed on a microbalance. The composition of the precipitate is $(CH_3O)_2C_{21}H_{20}O_2N_2.2CdBr_2.2HBr$; the conversion factor for cadmium is 0·092. The volume of the original solution taken should not be more than 10 ml.

Aluminium alloys are dissolved in hydrochloric acid and evaporated down with 3 ml. of sulphuric acid until sulphur trioxide is formed. The residue is taken up with hot water, and the solution is evaporated to 10 to 20 ml. after separation of the silica. The method for magnesium alloys is then followed.

Results of numerous test determinations are tabulated. In these, satisfactory results were obtained with amounts of approximately 0·25 g. of magnesium alloy and 0·3 or 0·5 g. of the aluminium alloy containing about 0·2 mg. of cadmium.
E. B. D.

Simple Apparatus for the Determination of Traces of Arsenic. E. Szép and W. Cieleszky. (*Z. anal. Chem.*, 1939, **116**, 34–38.)—The authors describe a cheap, efficient apparatus for the determination of arsenic by the method of Bodnár, Szép and Cieleszky (ANALYST, 1939, **64**, 300). Although the train is considerably simpler than the complicated apparatus used by Gangl and Sánchez, the results obtained are shown to be as reliable. For constructional details, reference should be made to the original paper. W. R. S.

Detection of Traces of Tellurium. L. Vignoli and A. B. Khaled. (*J. Pharm. Chim.*, 1939, **29**, 148–158.)—The reagent-solution used contains 100 g. of sodium hypophosphite, 200 ml. of water and 150 ml. of conc. sulphuric acid. One ml. of water containing the trace of tellurium as sodium tellurate is introduced into a test-tube and 2 ml. of the reagent are added. The liquid is heated to boiling over a flame; the flame is then removed, and 20 drops of conc. hydrochloric acid are added from a pipette to the tube held in a slanting position, so that the acid runs down the glass and forms a layer on top of the solution. A greyish-black ring of tellurium forms almost immediately at the zone of contact; the smallest amount of tellurium detectable is 0·0025 mg. Tellurium present as a tellurite is partly precipitated in the liquid before the addition of hydrochloric acid, and it is, therefore, necessary previously to oxidise tellurite with permanganate. Iron in the solution causes a strong yellow colour, due to ferric chloride, to develop at the zone of contact; if, however, the liquid is warmed gently the yellow colour is discharged and the tellurium ring develops. Selenium interferes by giving a general, but incomplete, precipitation of red selenium in the liquid; investigation, with a view to overcoming this difficulty, is in progress. Arsenic also gives a ring-test under the same conditions as tellurium; the ring is brown, and it is interesting to note that arsenic does not interfere, because in presence of tellurium two quite distinct rings are formed—an upper brown ring of arsenic and a lower grey ring of tellurium; this could be perceived with 0·005 mg. of both elements present. Bismuth interferes by giving a black precipitate prior to the hydrochloric acid addition; bismuth can be separated from tellurium by precipitation with hydrogen sulphide. Antimony is completely precipitated when the solution is heated with the reagent alone for half-an-hour on a water-bath; the tellurium test can be carried out on the solution after filtering off the antimony. Roughly quantitative results for tellurium can be obtained by employing standard conditions of heating and so on.
S. G. C.

Volumetric Determination of Aluminium in Citrate Solution. A. C. Titus and M. C. Cannon. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 137–140.)—A quantity of aluminium sulphate or potassium alum containing 0·08 to 0·43 g. of aluminium is dissolved in 50 ml. of water. The first portion of 25 ml. is treated with 6 g. of potassium fluoride and titrated with 0·5 N carbonate-free sodium hydroxide solution against phenolphthalein. This titration gives free acidity.

To the other 25-ml. portion are added 25 ml. of 0·610 *M* sodium citrate solution and the amount of 0·5 *N* sodium hydroxide solution employed in the first titration. The liquid is diluted to 100 ml., kept at the boiling-point for 5 minutes, cooled and titrated with the 0·5 *N* alkali solution after addition of 15 drops of alcoholic 0·075 per cent. thymolphthalein *plus* 0·025 per cent. phenolphthalein solution until a rose-coloured end-point is obtained. The following formulae are used in calculating the aluminium content:

For pure aluminium salts: Millimoles Al = millimoles NaOH × 0·697—0·341.

For potassium aluminium sulphate: millimoles Al = millimoles NaOH × 0·674 —0·317, potassium, but not sodium, having a slight effect on the reaction.

In either formula, mg. Al_2O_3 = millimoles Al × 50·97. W. R. S.

Determination of Chromium in Aluminium. L. Schönlau. (*Chem.-Ztg.*, **1939, 63, 140–141.**)—The customary method of dissolving the aluminium in sodium hydroxide solution is employed. The chromium is stated to remain in the insoluble residue along with iron, etc. The residue is filtered off, ashed, and fused with sodium peroxide; this converts chromium into chromate, which is determined by titration in the ordinary way. S. G. C.

Gravimetric Determination of Zirconium by means of Atoxyl. R. Chandelle. (*Bull. Soc. Chim. Belg.*, 1939, **48**, 12–32.)—Atoxyl (sodium *p*-aminophenylarsinate) quantitatively precipitates zirconium from chloride solution which is 0·5 *N* acid. The flocculent voluminous white precipitate can be converted into zirconia by ignition in air, in hydrogen, and again in air, as previously described for the precipitate obtained with methylarsinic acid (ANALYST, **1937**, **62**, 899). The procedure permits of the determination of zirconium in presence of zinc, manganese, nickel, cobalt, aluminium, copper, calcium, magnesium, and chromium, but titanium is co-precipitated. Iron also interferes; the author eliminates it by extraction with ether, and determines the last traces of iron in the weighed zirconia by colorimetry (*cf.* ANALYST, **1938**, **63**, 139, 452). W. R. S.

Titrimetric Determination of Magnesium. G. Szamek. (*Chem. Weekblad*, **1939, 36, 168–169.**)—An excess of 0·1 *N* barium hydroxide solution is added to a neutral solution of the sample containing the equivalent of not less than 0·01 per cent. of MgO and from which the members of the first three (analytical) groups of cations have been removed. The solution is boiled for 1 minute, a slight excess of 0·1 *N* zinc sulphate solution is added, and the mixture is back-titrated at the boiling-point with 0·1 *N* barium hydroxide solution, a 0·5 per cent. solution of thymolphthalein in alcohol being used as indicator (*cf.* T. Blasweiler, *Papier-Fabr.*, **1921, 19,** 425; R. Sieber, *id.*, **1923, 21,** 235). The difference between the sum of the volumes of the barium hydroxide solution used for precipitation and back-titration, and the volume of zinc sulphate used gives the volume of the former equivalent to the magnesium present; 1 ml. of 0·1 *N* barium hydroxide solution ≡ 0·002016 g. of MgO. Zinc sulphate is preferable to lead nitrate for the precipitation, as lead salts are readily hydrolysed, and sulphates and chlorides (which are also precipitated by lead) must be absent. Thymolphthalein is preferable to phenolphthalein. If the concentration of the sample is equivalent to less than 0·1 per cent. of MgO, or if too much barium sulphate is present (*e.g.* as the result of adding too great an excess of the reagents), the end-point is not sharp. It is then advisable to titrate by the light of a blue lamp, or to observe the colour after allowing the precipitate to settle. With concentrated solutions calcium hydroxide will also be precipitated and introduce an error. Recorded errors for solutions of magnesium sulphate containing the equivalent of 0·0017 to 0·0850 g. of MgO are 0 to 13·7 (mean, 5·7) per cent. With solutions equivalent to 0·0017 to 0·0170 g. of MgO and containing 0·06 to 0·02 g. of CaO, the errors were 7·1 to 17·6 (mean, 12·2) per cent. J. G.

Determination of Fluorine in Natural Phosphates and Phosphatic Fertilisers. D. S. Reynolds and W. L. Hill. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 21–27.)—An improved form of the Willard and Winter distillation method is proposed. A 0·5-g. sample is distilled with 15 ml. of dilute perchloric acid (2 + 1) at 125° to 150° C., by the use of the steam-distillation process described by Reynolds, Kershaw and Jacobs (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 156); 150 ml. of distillate are collected. If the sample contains pyrites or organic substances such as cottonseed meal, 2 to 3 ml. of saturated potassium permanganate solution are added prior to distillation. The distillate is neutralised to phenolphthalein with sodium hydroxide and diluted to 250 ml. To a 50-ml. aliquot part, 5 drops of alizarine indicator (0·1 per cent. solution of sodium alizarine sulphonate) are added, and the pink colour is discharged with *N* hydrochloric acid; 2·5 ml. of monochloroacetic acid buffer solution (a mixture of equal volumes of 0·8 *N* monochloroacetic acid solution and 0·4 *N* sodium hydroxide solution) are added, and the solution is titrated with 0·04 *N* thorium nitrate solution (1 ml. ≡ 0·75 mg. of fluorine, approximately). No alcohol is required in the titration liquid. The thorium nitrate solution is standardised by similarly titrating a known amount of sodium fluoride. The deduction of a "blank" obtained by carrying out the complete method, with the omission of the phosphate sample, is advised.

S. G. C.

Direct Titration of Sulphate. W. V. Burg. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 28–30.)—Sulphate may be titrated with lead nitrate in the presence of erythrosin as adsorption indicator, as follows:—The sulphate solution (50 ml.) is rendered very slightly acid with nitric acid, and 16 ml. of ethyl alcohol and 14 drops of indicator (1 per cent. aqueous solution erythrosin B) are introduced. Lead nitrate solution (0·1 *M*) is run in slowly, drop by drop, with constant shaking. The end-point is indicated by a violet colour of the liquid. Good results were obtained with from 0·05 to 0·19 g. of potassium or sodium sulphate. Owing to the low solubility of lead chloride in the alcoholic liquid, all but small quantities of chloride interfere with the method. It was found feasible, however, to titrate sulphate after a preliminary titration of chloride with silver nitrate and fluorescein adsorption indicator, the coloured silver chloride being filtered off. Nitrate does not interfere. The method is suggested as being worthy of further study with a view to extending its applicability to a wider range of amounts of sulphate.

S. G. C.

Microchemical

Micro-method for the Quantitative Determination of Sugar Alcohols. W. R. Todd, J. Vreeland, J. Myers and E. S. West. (*J. Biol. Chem.*, 1939, **127**, 269–273.)—Five ml. of the solution containing the sugar alcohol (0·1 to 0·7 mg.) are transferred to a Pyrex tube (25 × 200 mm.) and 3 ml. of a 1·08 per cent. potassium ferricyanide solution are added, followed by 3 ml. of a 5 per cent. solution of sodium sulphate in 3·33 *N* sodium hydroxide solution. The tube is immediately covered with a glass bulb; after the contents have been mixed, it is placed in a boiling water-bath for exactly 30 minutes and then cooled in a cold water-bath. Five ml. of a freshly made 1: 1 mixture of glacial acetic acid with "15 per cent. zinc acetate and 12 per cent. potassium iodide in combined solution" are added from a rapid-delivery pipette, and the liberated iodine is titrated with 0·005 *N* sodium thiosulphate solution, starch indicator being added near the end-point. A blank determination is made at the same time. The relation between the concentration of sorbitol, mannitol or other alcohols and the titration difference is not linear, and a curve must therefore be prepared for the calculation of the results.

To determine sorbitol in urine, 10 ml. are added to 75 ml. of water, and 15 ml. of a 28 per cent. solution of mercuric sulphate in 2 *N* sulphuric acid are added. The mixture is neutralised with barium carbonate (about 28 g.) and filtered. Zinc dust (1 g. per 15 ml. of filtrate) is added to the filtrate to remove traces of mercury, and the solution is again filtered. The filtrate, suitably diluted, is used to determine sorbitol as described above.

To determine sorbitol in blood, 5 ml. are added to 90 ml. of water, and, after laking is complete, 5 ml. of the above mercuric sulphate reagent are added and the mixture neutralised with about 9 g. of barium carbonate, after which the procedure is the same as with urine.

The presence of glucose in the blood leads to a change in the reducing equivalent of sorbitol and other alcohols, and corrections must then be applied. This is effected by determining the glucose equivalent in blood filtrates free from sugar alcohols and then determining the reduction in another filtrate of the same blood after the addition of known amounts of a sugar alcohol. By means of this device, recoveries ranging from 85 to 105 per cent. of added sorbitol or mannitol were regularly obtained. F. A. R.

Microchemistry of Yohimbine. A. Martini. (*Mikrochem.*, 1939, **26**, 227–232.)—The cyanide reaction is the most sensitive known for yohimbine. A small particle of potassium cyanide is added to a drop of a solution of yohimbine hydrochloride (1: 1000), and the mixture is slightly warmed. On cooling, long prismatic crystals, grouped in characteristic bushlike shapes, are formed. As little as 2γ of yohimbine may thus be detected in a dilution of 1: 5000. Characteristic crystals are also obtained with the following salts:—$Na_2B_4O_7,10H_2O$, Na_2SeO_3 and Na_2TeO_3 also down to a dilution of 1: 5000, and crystals are obtained with $K_2C_2O_4.H_2O$ down to a dilution of 1: 3000. Conversely, yohimbine may be used for the detection of the above-named salts. J. W. M.

Colorimetric Determination of Starch. J. J. Chinoy. (*Mikrochem.*, 1939, **26**, 132–142.)—The starch-iodine method is used. If the iodine is generated gradually in the solution containing starch, the starch iodide is not precipitated but remains as a blue colloidal solution. Iodine is liberated in a neutral or weakly acid solution by the addition of 2 to 3 ml. of 0·1 *N* potassium iodide solution and 1 to 2 ml. of 3 per cent. hydrogen peroxide. The mixture is made up to a definite volume (10, 25 or 50 ml.) and left for one hour, after which the excess of iodine is extracted by successive additions of 5 ml. of chloroform. The blue colours are then matched in a colorimeter (*e.g.* Kletts "Bio-model"). As little as 0·5 mg. of starch was determined with errors of 2 to 3 per cent. The method is applicable to the determination of potato, rice and wheat starches.

J. W. M.

Differentiation Reactions for Cocaine, Novocain and Stovain. A. Martini and J. C. Baró Graf. (*Mikrochem.*, 1939, **26**, 233–240.)—After a critical study of the various known reactions for the identification of these three compounds, the following three reagents are recommended:—potassium lead iodide (K_2PbI_4), rhodium chloride–potassium iodide ($RhCl_3KI$) and bromine water. With the first-named reagent all three compounds react to give colourless crystals of differing character. With rhodium chloride–potassium iodide novocain does not react, whilst cocaine gives short yellowish needles and stovain crystals of irregular form. With bromine water only novocain reacts, giving fine needle-shaped crystals. By the use of all three reagents the three compounds can be identified with certainty. Seven photomicrographs are given. J. W. M.

Anthranilic Acid as Reagent for the Microchemical Detection of certain Metals. O. G. Sheintzis. (*J. Ob. Chimie*, 1938, **8**, 596–601.)—Anthranilic acid gives characteristic crystals with cupric and mercurous salts and with salts of palladium, zinc and silver. The reaction is extremely sensitive, large crystals are formed, and these metallic ions can be detected in the presence of other metals (with the exception of cobalt, ferric iron and cerium, which are precipitated) and of one another. To a drop of the test solution on the slide there is added a drop of a 0·5 per cent. aqueous solution of anthranilic acid and the precipitate formed is examined under the microscope. The crystals obtained, slides of which are illustrated, are as follows:—Cupric anthranilate (prepared from the sulphate) gives pale green oblong hexagons and prisms (with dark ends) which coalesce to form rosettes; diameter 30 to 40μ. Mercurous anthranilate (prepared from the nitrate) forms aggregates which resemble brooms and consist of fine colourless needle-shaped crystals (rhombic system); diameter 200μ, the precipitate when first formed is yellow and amorphous. Palladium anthranilate (prepared from the chloride) gives yellow four-rayed stellar crystals in globular aggregates; diameter 5 to 10μ. Zinc anthranilate (prepared from the sulphate) is appreciably soluble. It crystallises in rosettes of rhombic and hexagonal crystals of the regular system; diameter 80 to 100μ. Silver anthranilate is more soluble than the salts of the other metals tested. The crystals, which form aggregates, are needles and prisms; diameter 100 to 150μ. The sensitivity of the reactions with the test solutions is:—copper, 0·013; mercury, 0·06; palladium, 0·015; zinc, 0·05; silver, 0·24γ. It is possible to detect one metal in the presence of the others as follows:—copper (1 part) in the presence of zinc (25 parts), silver (40 parts) and mercury (40 parts) taken together; sensitivity 0·08γ. Mercury (1 part) in the presence of copper (30 parts), zinc (30 parts) and silver (60 parts) taken together; sensitivity 0·06γ. E. B. D.

New Test for Lead. C. Mahr. (*Mikrochem.*, 1939, **26**, 67–71.)—Lead is detected by the formation of characteristic crystals of lead-thiourea nitrate. The reaction is extremely selective, only thallium and some of the platinum metals giving similar crystals. *Detail*—The test solution is evaporated to dryness on a microscope slide, which is then heated to volatilise any free acids and excess of mercury salts. The residue is taken up in 1 drop of 2 *N* nitric acid, and a little powdered thiourea (about 10 per cent. of the volume of the liquid) is added. Under the microscope (100×) the long (20–50μ) thin needle-shaped prisms may be observed at once. In presence of an excess of silver or copper foreign crystals of different form may be seen. If excess of foreign metals, especially silver, bismuth or copper is present, it is advisable to electrolyse about 0·5 to 1 ml. of the nitric acid test solution. The electrolysis is carried out at 3·2 volts and 0·2 amp. in a small platinum spoon with a bent platinum wire (1 mm.) as anode. A little ammonium nitrate is added, and the solution is gently warmed. The lead is deposited on the anode, which is then washed and dipped in 2 *N* nitric acid on a microscope slide, and thiourea is added as before. In pure solution the limit of identification is 0·02γ of Pb and the concentration limit 1 : 40,000. The method is especially useful for the detection of lead in alloys. J. W. M.

Detection of Silver, Lead and Mercury without Separation. B. Berisso. (*Mikrochem.*, 1939, **26**, 221–226.)—Silver, lead and mercury, when present together in the form of soluble salts, may be detected microscopically without separation if the ratio of the cations is such that the amount of silver or lead present is not less than 1 per cent. of the amount of either of the other cations, and the amount of mercury present is not less than 10 per cent. of the amount of the other cations. A drop of the test solution is divided into three portions. In one portion the silver is identified as the chromate crystallised from a very dilute nitric acid solution; in the second, mercury is identified as cobalt-mercury thiocyanate; in the third, lead is identified as the triple nitrite of copper, lead and potassium. Alternatively, silver may be identified either as silver chloride or as the triple chloride of silver, gold and rubidium; lead may also be identified as sulphate. J. W. M.

Physical Methods, Apparatus, etc.

New Spotting-Plate Test for Demonstrating the Effects of Extreme *p*H and *r*H Values. M. Déribéré. (*Ann. chim. anal.*, 1939, **21**, 63–66.)—The apparatus consists of a Pyrex glass plate with 9 depressions arranged in 3 rows and numbered 1 to 9. The base, which is removable, consists of a piece of cardboard covered on one side with aluminium paint or foil, and on the other with Chinese ink, so that alternative backgrounds are provided. The depressions in the first row contain 1 drop of a strong oxidising agent whose *r*H exceeds 41 (*e.g.* hydrogen peroxide or sodium hypochlorite) with 1 drop, respectively, of an acid whose *p*H is less than 3 (*e.g.* 0·1 *N* hydrochloric acid); of distilled water; and of an alkali whose *p*H exceeds 12 (*e.g.* 0·1 *N* sodium hydroxide solution). In each member of the next row is placed 1 drop of distilled water with acid, water and alkali as specified above; the third row contains a reducing agent whose *r*H is less than 18 (*e.g.* sodium hydrosulphite) together with these same 3 reagents. The test is made by introducing a drop of the solution to be tested into each depression and observing the results (*i.e.* the colour, the formation of any precipitate or both) in ordinary light on a white background, and in filtered ultraviolet light against the black and aluminium backgrounds. With some solutions the tests may be carried out on filter-papers. It is thus possible to observe the behaviour of the solution under test at the ends and the middle of wide *p*H and *r*H ranges, and to use the results as an aid to identification. Details are given for methylene blue, methyl violet, fuchsine, crocein, rhodamine, rose bengal, erythrosine, flavin, diazol yellow, acridine orange, naphthionic acid, Neville-Winther acid and Schaeffer's salt. Applications to the examination of pharmaceutical products, extracts of vegetable colouring matters and tanning extracts are also indicated. J. G.

Evaluation of Leather by means of X-ray Diffraction Patterns. R. C. Bowker and H. J. McNicholas. (*J. Amer. Leather Chem. Assoc.*, 1939, **34**, 101–102.)—D. J. Lloyd (*J. Int. Soc. Leather Trades' Chem.*, 1935, **19**, 345) has published X-ray diffraction patterns of good and poor leathers from different sources. It was observed (*id.*, 1934, **18**, 22, 68, 307, 562, 600) that, compared with the good leathers, the rings in the patterns from the poor leathers (and especially the outermost ring) were poorly defined, and these differences were attributed to structural differences in the more highly-organised regions of the fibre. Recent methods for the measurement of the effective acidity of leather (see Bowker and Wallace, *J. Amer. Leather Chem. Assoc.*, 1933, **28**, 125) have enabled the mechanism of the deterioration of leather by acid to be studied (see Kanagy, *id.*, 1937, **32**, 12), and this work has also provided authenticated samples for the present experiments. These samples were originally tanned with chestnut-wood or quebracho-wood extract, with and without treatment (immediately after tanning) with sufficient sulphuric acid to add 4·2 and 4·9 per cent., respectively, to the sulphuric acid content. The initial *p*H values were 3·8 and 5·4 for the untreated chestnut and quebracho leathers, and 1·8 and 2·0 for the corresponding acid-treated leathers, respectively. The corresponding changes in strength after 2 years were —6·8, +5·5, —60·6, and —47·7 per cent., and the soluble nitrogen contents after 11 years were 12·0, 3·1, 100·0 and 91·0 per cent., respectively. Hand-inspection showed that deterioration was very marked for the acid-treated leathers, which could be powdered in the hand, whilst the original high quality of the others appeared to have been maintained to a large degree. The X-ray diffraction patterns for all 4 leathers are reproduced in the original. Unfiltered radiation from a copper target operated at 35 peak-kilovolts was used, the records being produced on a flat film at a distance of 62 mm. from the sample. It is shown that the patterns were essentially the same in every instance, the only significant difference being the somewhat better definition of the outer ring obtained with the deteriorated specimens. The results suggest that further work is required before the method can be used with safety for judging the condition of leather. More differences appear to exist between the patterns of leathers tanned with the different materials (*cf.* Jordan Lloyd, *loc. cit.*) than exists between those of good and acid-deteriorated leathers which have been tanned with the same tanning agent. J. G.

Observations on Flame Spectra. T. Török. (*Z. anal. Chem.*, 1939, **116**, 29–33.)—A simple improved procedure for carrying out a flame test without a platinum wire consists in placing a Bunsen burner in a horizontal position over a porcelain crucible containing the strongly acid chloride solution to be tested and a few pieces of zinc. Minute droplets of the solution are projected into the flame by effervescence, producing a continuous extensive coloration of the flame. If the solution contains heavy metals precipitated by zinc, a strong solution of ammonium carbonate may be added, drop by drop, to the acid chloride solution from a burette placed above the horizontal flame.

The literature on qualitative analysis contains no reference to the fact that the phosphates of the alkaline earths do not give the well-known flame reactions. It is necessary to moisten the test substance on a platinum wire with strong sulphuric acid, and heat it in the reducing flame to convert the resultant sulphate into sulphide. Subsequent treatment with hydrochloric acid will cause a positive reaction to be obtained. W. R. S.

Method of Testing the Durability of Bituminous Road Binders. H. C. Bennett and D. W. Parkes. (*Chem. and Ind.*, 1939, **58**, 201–202.)—Retention of ductility is considered to be the most important characteristic of a road binder which may be used to correlate laboratory data and service performance. This was justified by preliminary tests in which the binder was spread in a film on rubber strips, and the degree of cracking of the film was observed after weathering and then stretching the rubber by hand. The film now used is 18 mm. square and 0·005 in. thick, and the weathering is carried out by placing the films absolutely level in a ventilated oven at 40° ± 0·5° C. An apparatus is described for measuring the critical temperature at which a film cracks when elongated 33 per cent. It consists of a small wooden cabinet, insulated against loss of heat, and provided with a glass top. It is divided horizontally into 2 halves by stout metal gauze. The top half contains the elongating mechanism, a fan (driven from outside) and a thermometer, whilst the bottom half is divided vertically by gauze into 2 compartments which are used for heating and cooling, respectively. Heat is provided by means of a carbon filament lamp which is shielded to protect the rubber strip from radiated heat, and is operated by a hand-switch. Carbon dioxide is used for cooling, and is admitted to the other chamber from an inverted cylinder through a fine-adjustment valve. Elongation to 33 per cent. is carried out by means of an automatic trigger operated by coil springs. In making a test the strip is placed in the grips, the trigger is set, and the temperature is maintained for 8 minutes at a value 5° C. higher than that at which cracking is expected to occur; the trigger is then released. If no crack appears the test is repeated 10 to 20 seconds after at a temperature 1° C. lower, and so on until the critical temperature is reached at which the film cracks completely. If each binder is weathered for five periods up to 72 hours, the curve relating the time and critical temperature may be used satisfactorily to indicate the behaviour of the binder in service, especially where the binder is used in a thin film and is subjected to the maximum atmospheric exposure. Thus, binders with high critical values and giving steep curves proved unsatisfactory. The test was also used to show that the durability of road binders is hardly affected by the viscosity or quantity of the oil used for "oiling-back" (within the range 100 to 300 seconds), but is greatly influenced by the quality of the oil. It was also shown that the deterioration which occurs when a heavy oil binder is stored at a high temperature is not revealed by standard distillation tests, but is shown by a high critical temperature in the strip test. The capacity of a film of aged binder to seal and allow re-consolidation after a severe strain, may also be measured by the strip test. J. G.

Reviews

PRACTICAL ORGANIC CHEMISTRY. By F. G. MANN and B. C. SAUNDERS. 2nd Edition. Pp. xiv + 418. London: Longmans, Green & Co., Ltd. 1939. Price 8s. 6d. net.

Sir Wm. J. Pope contributes a foreword to this volume in which he emphasises the importance of attention to details and precision in carrying out experimental work, especially in organic chemistry. Such attention frequently makes all the difference between failure and success of an experiment, and it is believed that, as a rule, too little regard is paid to it by teachers. In assessing the value of any new addition to a section of the literature of chemistry which is already well provided for, one looks principally for special features that distinguish the newcomer from its fellows. This attention to detail is the most important of such features in the present instance, and although at times it may convey the impression of prolixity to the older chemist, there is little doubt that it will prove of great value to the students of the B.Sc. course standard for whom the book is primarily intended.

Other special features of which mention might be made are that every experiment described has been carried out repeatedly by, or under the eyes of, the authors, and therefore is guaranteed to "work" if the directions are followed; also that particular attention has been given to simplification in technique and economy in apparatus and chemicals. The descriptions of the experiments are preceded by short accounts in small print of the chief theoretical considerations involved.

On the whole, apart from these features, the book follows conventional lines. Thus methods and manipulation are first considered and are followed by preparations, which occupy some 160 pages. The following 160 pages are of most interest from the point of view of the analyst, as they deal with qualitative and quantitative organic analyses. Micro-methods are purposely omitted, but not all will feel that this course is justified by the reasons given, namely, that micro-methods find no place in many laboratories and that macro-quantitative methods are an excellent introduction to micro-methods. The book concludes with simple enzyme reactions, and appendixes dealing with reagents, first-aid, methods of combatting fires of various kinds, and tabulated data referring to the physical and chemical properties of common substances.

There is little that calls for special note in the analytical section, as the methods described follow well-trodden paths. No mention is made of the use of a catalyst in the wet-oxidation operation of the Kjeldahl process, and consequently certain substances for which, according to the author, the method is suitable, would give low results if the technique described were followed. In the same method the desirability of direct distillation from a 750-ml. flask containing only about 100 ml. of liquid, as compared with steam-distillation, may also be questioned. The instruction to shake *thoroughly* when carrying out an extraction with ether, might be modified to allow for circumstances in which such treatment would result in an obstinate emulsion.

Points such as these, however, can easily be rectified in a future edition, and to judge from the fact that the book has reached its second edition in less than three years, this should soon be required. The book is well-produced, the 64 diagrams being small but clear, and the price is most reasonable. It should prove a good investment to those responsible for classes in practical organic chemistry of degree standard. JULIUS GRANT

OUTLINES OF METHODS OF CHEMICAL ANALYSIS. By G. E. F. LUNDELL, Ph.D., and JAMES ERVIN HOFFMAN, Ph.D. Pp. xi + 250. New York: John Wiley & Sons; London: Chapman & Hall. Price 15s.

How great the need has been for some such book as this cannot perhaps be fully realised until one compares it with the ordinary stereotyped kind of text-book of analytical chemistry. The volume contains 53 chapters and is divided into 5 parts. The first 12 pages give a very brief account of modern views on the structure and the classification of atoms; then follows a chapter on the occurrence of the elements in nature and in materials; a chapter on sampling and one on the preparation of the solution for analysis complete Part I. Part II deals with the theory and practice of the ordinary group separations; there are also chapters treating of special methods of separation within the hydrogen sulphide and ammonium hydroxide groups and of separations by ether extraction, mercury cathode, and so forth. Part III discusses certain gravimetric methods of the ordinary type and six of the principal ones using organic reagents; then follow accounts of volumetric methods (those selected including acidimetric, oxidation-reduction, iodimetric and potentiometric), electrolytic and colorimetric methods and finally a brief chapter on spectrography. Part IV gives diagrammatic schemes of analysis for a variety of substances, ranging from limestone to bronze. Part V discusses probable error and related matters, and the evaluation of results (including those of a number of analysts). There is a final chapter on standard analysed samples.

When it is borne in mind that the whole of this mass of material occupies only 232 pages, the feeling must inevitably arise that, however extreme the condensation, the space allotted is so inadequate that the book can serve no useful purpose. The answer to this is that it is not an ordinary text-book of analytical chemistry; it does not attempt to describe how a given operation should be carried out and it takes for granted a great deal of "student" knowledge. It does, however, provide a great mass of information which is not readily accessible (sometimes not accessible at all) in the ordinary text-books; this information is frequently, one might say generally, the reverse of encouraging to the beginner, including, as it does, notes on incomplete precipitation, co-precipitation, hindrance of precipitation and interference of all kinds. It might be commended as a corrective and as calculated to induce that "fear of the Lord" (sometimes called "scientific humility") which is "the beginning of wisdom" both in those who have "finished analytical chemistry" in a one-year course and in those teachers who have persuaded them that they have so finished.

Among the many unusual features of the book is the extensive use of a novel form of table which has much to recommend it. Each table (some 80 in all) takes the form of the symbols of the elements arranged as in the periodic system; elements which exhibit the property under discussion are surrounded by a block, other elements which, by co-precipitation or some other form of interference, require taking into consideration, are surrounded by other types of block, the number of types used running up to four in many tables. It is surprising to note how relatively compact these blocks are even when dealing with the most diverse properties. The most unsatisfactory chapter is probably that on colorimetric methods; in the four pages allotted one cannot expect any very elaborate treatment, but much might have been made of a general discussion, instead of which we have accounts of three rather limited methods. Even so, the selection seems peculiar, the methods being: (*a*) colours formed with hydrogen peroxide in acid solution, (*b*) in alkaline solution, (*c*) colorimetric determination of aluminium with aurin-tricarboxylic acid.

The names of the authors are a guarantee that the methods given throughout the book are sound, but lack of reference to Dr. Schoeller's methods for tantalum, niobium and their associates weakens much that is said about these elements. Amongst the causes of error that might be profitably included in a subsequent edition are the adsorption of tin on precipitated metallic antimony (p. 214), and the danger of co-precipitation of cobalt with the zinc oxide precipitate (p. 90).

The book is apparently primarily intended to be supplementary to Hillebrand and Lundell's *Applied Inorganic Analysis*. Printing, proof-reading and binding are alike excellent, and the index of 17 pages seems adequate. The authors' chief aims are stated to be: "(1) to furnish analysts with information concerning the behaviour of all the elements in the more important reactions used in analytical chemistry; (2) to stimulate searches for more selective reagents; (3) to enlighten chemists who hold chemical analysis in too light regard; (4) to inform non-chemists concerning the complexities and difficulties that beset the analyst." This fourfold aim is possibly responsible for the principal disadvantage under which the book labours—the extreme condensation; one wonders whether the two latter aims are not perhaps somewhat incompatible with the two former, and whether anything will induce "chemists who hold chemical analysis in too light regard" to read sufficient to produce "enlightenment," while for "non-chemists" it will be tough reading indeed. It is easy to criticise, however, and hard to remedy; whatever the aims and whether or no they have been achieved, the authors have produced a notable work which is in many respects unique in its masterly survey of all the factors influencing certain analytical reactions and in its concentration upon analysis rather than determination. Unique, too, in that within an all too brief compass it contrives to give so much information that, as a rule, only the years can give and to bring the fruits of long experience within the covers of a narrow book.

B. S. EVANS

TABELLEN UND VORSCHRIFTEN ZUR QUANTITATIVEN ANALYSE. By W. D. TREADWELL. Pp. 284, 126 Figures in Text. Leipzig and Vienna: Franz Deuticke. Price RM.9.

The title aptly describes the book, tabular form being adopted in many places, and an immense amount of information being compressed into its two hundred and eighty-four pages. This result is obtained by the adoption of a style that the reviewer can describe only as that of the student's notebook.

Methods are arranged under the headings of solution, precipitation, filtration, washing, formula of precipitate, and method of determination, with occasionally a reference to the literature. A few concise phrases give the facts.

In this manner, for the cations, two hundred and five separations and determinations by chemical methods are covered in forty-nine pages, and one hundred and three by electro-analytical methods in thirty-four. One hundred and seven separations and determinations for anions are given in twenty-eight pages. A section of six pages is devoted to the cupellation of precious-metal alloys. This is followed by twenty-four pages on separations by distillation, and then eight pages on elementary analysis. The final section is one of fifty-two pages on gas analysis.

This compression of much material into little space confers both advantages and disadvantages. It is very easy to find information in the book, but this information must, of necessity, be lacking in explanatory detail. Thus, while it will make a valuable addition to the library of the experienced worker, it might be even dangerous in the hands of one not so experienced. It must be accepted with caution, as among the many excellent methods given are a number that are no longer regarded as accurate, and no indication of relative dependability is given. It conveys the impression that analytical reactions are clear-cut and not subject to interference, and that methods of separation always have the same efficiency, irrespective of the relative concentrations of the ions present.

This book is worth its place as an addition to any analytical library, but it would be unwise to replace by it other books of less scope which are able to give more detail.

K. F. ALLEN

AN INTRODUCTION TO INDUSTRIAL RHEOLOGY. By G. W. SCOTT BLAIR. Pp. xiii + 143. London: J. & A. Churchill, Ltd. 1938. Price 7s. 6d. net.

Rheology is an American term which the author of this book defines as the science of the flow and deformation of matter. All materials suffer deformation and many flow, when stressed. At the one extreme is the true liquid, which flows when acted on by a force, however small, and of which the coefficient of viscosity is independent of the stresses used in measuring it; at the other extreme is the perfectly elastic material, which returns to its original dimensions immediately on the removal of any applied stresses. Between these two extremes lie a great number of the materials used in everyday life.

The author's discussion of the various rheological phenomena is illustrated by reference to substances by which they are exhibited. Some idea of the many fields in which these rheological effects are of practical importance may be gathered from the headings to Chapters VII and IX—"Ostwald's Theories of Structural Viscosity and Structural Turbulence, The Ostwald de Waele Equation—Its Application to Dyestuffs, Cellulose Derivatives, Amalgams, Fats, Solders, Soaps, Oils and Bitumens, Milk and Cream," and "Series Flow Equations, Elastic Hysteresis—Applications to Rubber, Silk, Wool, Hair, Fibres, Cheese, Road Foundations, Nitrocellulose, Flour Doughs, and Metals."

The aim of the book is stated on the second page. It is to bring together the published work on rheological methods for practical purposes, while including no more theoretical physics than is essential for the practical man. It is doubtful, however, whether a practical man would derive much benefit from the statement "extensimeters are in general very difficult to design." This is true but not very helpful. There is, too, a lack of lucidity in some of the theoretical work; for example, the derivations of Poiseuille's law and the equation for the concentric cylinder viscometer (co-axial is the better term) are unsatisfactory, and it would have been better to refer the reader to some standard text-book such as Poynting and Thomson's *Properties of Matter.*

Unfortunately in such a small book it has not been possible to include a very critical discussion of the ground covered, and in some instances the comments on publications to which reference is made are so brief as to be misleading. For example, Andrade's theory of the viscosity of liquids is said to be based on the idea "that there is a momentary combination of neighbouring molecules and that in viscous flow these groups are broken down and the molecules change partners." Again, in the note on Chalmer's work on the boundary layer between metallic crystals the author appears to have misunderstood the scope of the investigation. Chalmer's work was not, as is here suggested, concerned with the explanation of the difference between the theoretical and practical strength of metals.

However, these defects are not such as would mislead a critical reader, and there is no doubt that the book should prove very helpful to those who are already concerned with the anomalous flow properties of any material, in giving an introduction to published work related to their own field of enquiry.

There is a glossary of rheological terms, and after each chapter there is a comprehensive bibliography, adding greatly to the value of the book.

Its chief value would appear to be that it brings together under one cover the diverse applications of rheological methods and stresses the "essential unity of the problems involved."

R. W. DOUGLAS

(1) INTRODUCTORY QUALITATIVE ANALYSIS. By WARREN C. VOSBURGH. Revised Edition. Pp. vi + 222. London: Macmillan & Co., Ltd 1938. Price 10s.

(2) QUALITATIVE CHEMICAL ANALYSIS. By LOUIS J. CURTMAN. Revised Edition. Pp. ix + 514. London: Macmillan & Co., Ltd. 1938. Price 16s.

(3) THEORETICAL QUALITATIVE ANALYSIS. By J. H. REEDY. International Chemical Series, edited by JAMES F. NORRIS. Pp. ix + 451. London: McGraw Hill Publishing Co. 1938. Price 18s.

The modern tendency in books on qualitative analysis is to devote an ever-increasing proportion of space to theoretical considerations at the expense of the treatment afforded to the reactions of ions and the systematic examination of unknown mixtures; in fact, it may be said with some justification that books on analytical chemistry are now quite as much over-balanced on the theoretical side as they were in the opposite direction at the date when Ostwald, by his insistence on the necessity for greater attention to theory in the teaching and practice of analytical chemistry, rendered his great service to that mixture of science and craftsmanship.

It may well be doubted whether any book that neglects, to take one instance, the misnamed "rarer" elements, and deals only with a selected list of anions and cations, can lay full claim to be a work on inorganic qualitative analysis.

It would appear that we have now reached a stage in the development of chemical literature when, if both aspects of this important subject are to receive the full and adequate treatment they deserve, they would be better treated under separate covers, and the reaction represented by the equation:

$$\text{Theory} + \text{practice} \rightleftharpoons \text{Chemist}$$

allowed to take place in the mind of the student—its most fitting medium.

This criticism is in no wise intended as a reflection on the quality of such descriptive matter as is contained in recent publications, which in the three books under consideration reaches a very high standard, but only on its restricted nature. Of these books, the first two are mainly true to type; the last, together with other recent books, shows signs of a return to more equal treatment.

One practical point inculcated by these and other American writers, namely, precipitation by hydrogen sulphide in a closed system, is worthy of wider imitation in this country.

(1) This short elementary course in practical qualitative analysis and general theory by Professor Vosburgh, in which the student is taken through a restricted and selected list of cations and anions, is of interest on account of a system of semi-micro technique that is treated in the text concurrently with the details of the usual qualitative manipulation. This early introduction of small-scale working

to the elementary student is combined with the use of a few organic co-ordination reactions in the group separations, and has much to commend it.

The ionisation and physico-chemical theories are treated according to the newer conceptions. The style is concise, and the explanatory matter lucid, this result being attained within the compass of 222 pages by careful selection of subject matter rather than by terseness of expression. No errors or misprints were noted.

On account of its restricted scope, the book, as a whole, would be more suited to those taking chemistry as part of a general course than to those whose studies are intended to lead to the practice of chemistry as a profession. It should be of much interest to teachers of elementary chemistry.

(2) This, the second edition of Professor Curtman's well-known book, has been reset and to a very large extent re-written—more particularly in the theoretical part, where the newer conceptions of ionisation, co-ordination valence and the theory of conjugate acids and bases receive adequate treatment.

The practical section, intended to cover a year's study of qualitative analysis, includes much of the author's work that has been already published in periodical literature, and thus constitutes a useful collection of scattered research papers on qualitative analysis. It is particularly noteworthy for a systematic scheme for anion analysis.

In common with most books written primarily for a particular group of students, it contains much matter of doubtful interest to a wider class of readers, except perhaps teachers.

The descriptive and systematic sections are confined to twenty-four metal ions. There is a short section on micro-manipulation adapted for use with the regular system, and a full description of the author's system for providing each student with a separate collection of reagents.

In a book that, in general, is so remarkably free from error of all kinds, the following slip, on page 40, is to be regretted. "The ionic theory of Arrhenius . . . explained why, during electrolysis, the cations should migrate to the anode and the anions to the cathode."

(3) The modest preface to Professor Reedy's book makes no claim other than it shall be a study book for students beginning analytical chemistry; in actual fact it goes very much further, and being written, despite its title, from the viewpoint of an operative chemist, is worthy of consideration by those who study chemistry as a means to an end, as well as those to whom it is part of a general education. It shows no evidence of having been specially written to suit the needs of any particular group of students, and discusses the rival merits of contending theories and procedures in a critical and well-balanced manner.

The book is written in an easy, in parts in a colloquial, and sometimes in an irritating, style; an excessive use of formulae in statements such as that on page 304, which conveys the information that NH_4^+, in the presence of $HC_2H_3O_2$, gives a white precipitate with $Na_2C_4H_4O_6$, is liable to induce an attack of mental hiccough in even a practised reader.

The treatment of metal ions is limited to twenty-four, but the groups into which a few of the commoner "rarer" elements fall is indicated. The book is not entirely free from errors; there is a zero missing in an equation on page 88, and

Table 37 has been reprinted on page 312 instead of the Table 38 described in the text.

The special claim of this book to a place in the somewhat over-crowded section of literature to which it belongs, is that it teaches theory from the angle of the man at the bench.

F. L. OKELL

A TEXTBOOK OF PHARMACOGNOSY. GEORGE EDWARD TREASE, B.Pharm., Ph.C., A.I.C., F.L.S. Third Edition. Pp. x + 740. London: Baillière, Tindall & Cox. 1938. Price 21s.

One of the greatest dangers that beset the chemist is that the close attention he must pay to the vast volume of literature published month by month may badly distort his sense of perspective. It is so very easy to fall into the error of regarding as important only work published during the last decade, and one is inclined to ignore or even to forget altogether the historical background of one's subject. The chemist employed in the drug industry for instance, especially if engaged in research work, may readily come to believe that the crude natural drugs that formed the beginnings of his particular science are no longer of importance, having been entirely superseded by synthetic drugs. For such a perverted outlook no better antidote can be imagined than the comprehensive volume under review. It will, of course, need no recommendation to pharmacists, most of whom are already very well acquainted with it, and it should be equally indispensable to those analysts who have to examine crude drugs and report upon them, not only because of the notes concerning the identification of individual drugs that are given, but also for the interesting historical, chemical and clinical data that accompany them. The book could easily have been merely a *catalogue raisonné*, but this danger has been successfully avoided.

By far the biggest portion of the book is occupied with individual descriptions of the chief drugs, arranged according to plant families. Each description comprises an account of the source, the method of collection and the preparation of the drug, with historical notes on the more important. This is followed by a description of the macroscopical appearance and microscopical characteristics, these being frequently illustrated by diagrams; particular emphasis is laid on those characteristics that are useful in the identification of an unknown specimen. The account is completed by a note regarding the drug's chief constituents and the uses to which it is put. It is on reading through this part of the book that one is struck by the large number of natural drugs that are still essential, in spite of the progress made by modern synthetic chemistry.

In addition to the main section, there are other parts treating other aspects of the subject. The first part consists of an historical introduction and account of the London drug market, a chapter on plant principles and their extraction, another on enzymes, and other chapters on the cultivation of medicinal plants and on their collection, drying and storage, and lastly one on insect pests. The second part of the book consists of five important chapters on microscopy, and there is another part that includes an account of the physical and chemical methods of drug analysis and fluorescence analysis.

This is unquestionably a book that should be on the shelves of all who have to handle crude drugs, and it should be considered as indispensable to pharmacists and analysts who have to deal with such material. It can be thoroughly recommended as a clear, concise, up-to-date account of the subject, with every evidence of having been carefully revised since the previous edition. It is well printed and bound and is furnished with a good index. F. A. ROBINSON

THE MICROSCOPICAL STUDY OF DRUGS. By LILIAN A. KAY, B.Pharm., Ph.C. Pp. viii + 228, with 47 Plates. London: Baillière, Tindall & Cox. Price 10s. 6d.

In the preface the author states that her aim in writing this laboratory manual has been "to provide a work dealing comprehensively with the practical microscopical examination of the drugs" included in the syllabus for the Ph.C. and B.Pharm. examinations, and which would also be an introduction to the subject for students preparing for the F.I.C. (Branch E) examination. The result is a most useful book showing unmistakable evidence of careful and painstaking effort, the plates in particular being of extraordinarily high merit. It is worth noting that all the plant drawings have been specially executed for this book. The volume opens with chapters on the drawing of sections, on micro-measurement and on the use of clearing solutions, macerating fluids, and reagents for identifying specific types of tissue. The rest of the book consists of a series of instructions for the mounting and examination, under the microscope, of thirty of the most important drugs, emphasis being laid on those characteristics that are most useful for identifying each one. Though these instructions are rather monotonous to the casual reader, they are excellently suited for their purpose. Each section includes a summary of the diagnostic microscopical characters of each drug and a plate illustrating its various tissues. These drawings are a model of what such drawings should be, and for them, apart from other features, the book is well worth having.

This is certainly a text-book that the student will wish to keep for reference when his examination is over, and that is a great deal more than can be said of many text-books!

There is an adequate index, and the type and binding are both good. The publishers are to be congratulated on producing such an excellent volume at a price that is very reasonable, considering the number of blocks that presumably had to be prepared specially for it. F. A. ROBINSON

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on May 3rd, the President, Professor W. H. Roberts, in the chair.

The following were elected members of the Society:—J. B. Firth, D.Sc., M.I.Chem.E., F.I.C.; G. Isles; C. H. Wordsworth, B.Sc., A.I.C.

Certificates were read in favour of the following candidates for membership:—D. O. Burgess; V. C. Marquez, D.Sc.; J. Kay; C. A. Macdonald, B.Sc., F.I.C.; A. Srinivasan, M.A.

The following papers were presented and discussed:—"Extract of Malt with Cod Liver Oil: Determination of Oil and Vitamin A," by D. C. Garratt, B.Sc., Ph.D., F.I.C.; "The Presence of Leuco-anthocyanins in Criollo Cacao," by the late A. W. Knapp, M.Sc., M.I.Chem.E., F.I.C., and J. F. Hearne, A.I.C.; "Notes on the Examination of Textiles in Cases of Suspected Dermatitis," by H. E. Cox, Ph.D., D.Sc., F.I.C.

SCOTTISH SECTION

An Ordinary Meeting of the Scottish Section was held in the North British Station Hotel, Edinburgh, on April 28th. Mr. T. Cockburn, the Chairman, presided over a large attendance of members and friends.

The following papers were read and discussed:—"Counterfeit Coins," by A. Scott-Dodd, B.Sc., Ph.D., F.I.C.; "The Assay of Mercury," by James Sandilands, F.I.C.; "Description of a Closed Respiration Apparatus for Plant Tissue," by A. M. Smith, Ph.D., D.Sc., A.I.C.

Death

We deeply regret to record the death of Kenneth Edward Nethercoate Williams, a member of the Society since 1923.

Obituary

RICHARD AUGUSTUS CRIPPS

RICHARD AUGUSTUS CRIPPS died after an operation in a nursing home at Hove on March 31st, 1939, at the age of 76.

Cripps was born at Goring, Sussex, and served his apprenticeship with Mr. J. H. Read, pharmaceutical chemist, Upper Holloway, London. In 1881 he was Jacob Bell Memorial Scholar of the Pharmaceutical Society, and in the following year was awarded that Society's bronze medal for practical chemistry. For two years he acted as demonstrator for Professor Attfield, and later became an assistant in the laboratory of Messrs. P. W. Squire.

In 1884 he passed the "Major" examination of the Pharmaceutical Society, and then became analyst to Messrs. Southall Bros. and Barclay, Birmingham. He was elected a Fellow of the Institute of Chemistry in 1888, and in 1893 set up in private practice as an analyst at Haywards Heath, Sussex. In addition to his consulting work he established, in 1895, a business as wholesale manufacturer of galenicals and concentrated infusions. This met with such success that in 1904 he opened extensive premises at Hove, and, in association with his son, Mr. R. D. Cripps, was able to extend its scope and ultimately to convert it into a private company.

Cripps was elected a member of our Society in 1896, and served on the Council in 1910–11. In 1901 he was appointed Public Analyst for the County Borough of Bournemouth, a post that he held for thirty-two years. His official work, however, occupied only part of his time, and he was able to do some original work. Between 1883 and 1928 he contributed fourteen papers to the *Pharmaceutical Journal*. To THE ANALYST he made four contributions: "Notes on the influence of Boric Acid upon the Action of the Digestive Ferments" (1897); "Examination of Cough Mixture" (1902); "The Determination of Essential Oil and Moisture in Spices and Aromatic Drugs" (1909); "The Presence of Sulphates in Flour" (1914).

The papers that he prepared for the British Pharmaceutical Conference included: "An Examination of some Commercial Concentrated Infusions" (1905); "Decoctum Aloes Co. Concentratum; Notes on the Research upon Ipecacuanha" (1895); "Notes on Unguentum Cocainae B.P." (1906).

He was the author of a book, *Galenic Pharmacy*, popular with students of pharmacy thirty or forty years ago. As founder of the Cripps Exhibition (value £21), tenable at The Brighton Technical College, he acted as examiner in conjunction with other pharmacists; also, at various times he read papers to the evening students on subjects so wide apart as: "Coal Tar Distillation and some of its Products," "Note on the New Pharmacopoeia, Tincture Deposits," and the "Estimation of the Alkaloids of Conium."

Such a wealth of work from one man speaks volumes for his energy. Cripps belonged, however, to the old school who, after a hard day's toil, thought nothing of staying late in order to clear up points that the work of the day had left obscure. For such men we, a younger generation, have much to be thankful.

My first acquaintance with him was through his great friend, the late Mr. E. H. Farr, pharmacist, of Uckfield, who at that time was examiner for the

Pharmaceutical Society. Later, Cripps and I often met, generally in opposition, both in and out of Court, but we always remained good friends whether the result was a win, a loss or a draw.

Cripps was a man of deep religious feeling. At his funeral, at which I represented our Society, no one could fail to be struck by the very large number of pharmacists present to pay their last tribute of respect. The impressive words of the officiating clergyman were an eloquent testimony not only to the high regard in which Cripps was held by his professional colleagues, but also to the affection felt for him by the members of the church he had so regularly attended, and in which he had taken such a practical interest. S. ALLINSON WOODHEAD

The Determination of Traces of Zinc in Biological Material and Natural Waters

BY NOEL L. ALLPORT, F.I.C., AND C. D. B. MOON, A.I.C.

(*Read at the Meeting, April* 5, 1939)

RECENTLY, considerable interest has attached to the determination of the minute traces of zinc now known to be widely distributed in plant and animal tissues and possibly playing a part in the biological economy. In the absence of suitable specific colour reactions it is necessary first to separate the zinc, and various proposals have been made to effect this by extraction with a solution of dithizone (diphenyl-thiocarbazone) in chloroform or carbon tetrachloride.[1,2,3] In our hands these methods did not prove to be satisfactory. Sylvester and Hughes[4] recommend extraction with a chloroform solution of dithizone from an aqueous medium buffered with ammonium acetate at about *p*H 4·5, and in the early stages of this work these conditions led to promising results. Later, when the determination of the isolated zinc had been perfected, this method of extraction was found to be unreliable, particularly for minute traces when relatively large proportions of heavy metals and iron were also present. Further, the method is inconvenient for the examination of natural waters without first resorting to preliminary evaporation of large volumes of the sample, which involves the risk of inaccuracies due to contamination by zinc from the vessels used.

Some years ago del Campo Cerdan and Puente[5] found that when resorcinol is added to an alkaline solution of a zinc salt and the mixture is protected from oxidation, a purple colour is produced. Although too limited in application to be satisfactory as a colour test, this reaction suggested that the presence of resorcinol might facilitate the extraction of traces of zinc from an alkaline medium by means of a chloroform solution of dithizone. Repeated trials have shown this supposition to be justified.

In the method here described, the zinc, together with any heavy metals, is extracted with dithizone from an alkaline tartrate solution containing resorcinol, and the metals are transferred from the chloroform solution of dithizone by shaking with $N/10$ hydrochloric acid. The heavy metals are removed by means of hydrogen sulphide, the filtrate is evaporated, and the zinc is precipitated with quinaldinic acid (α-quinoline carboxylic acid) according to the method of Rây and Bose.[6] The precipitate of zinc quinaldinate is exceptionally granular and easy to manipulate. If a microchemical balance is available the determination may be completed gravimetrically; alternatively, the colorimetric method which we describe has proved to be quite convenient for quantities of zinc ranging from 5 to 50γ. The various suggestions for the colorimetric or titrimetric determination of minute quantities of zinc with dithizone[3,7,8,9,10,11,12] either failed to give reliable results or were inapplicable to this particular work. Loss of zinc by adsorption during the removal of heavy metals as sulphides[13,14] was prevented by precipitating from a mixture composed of equal volumes of $N/10$ hydrochloric acid and acetone.

METHOD.—*Reagents.*—Water and all chemicals should be of analytical reagent quality. The solution of dithizone in chloroform must be specially purified not more than two days before use in the following manner:—Dissolve 0·1 g. of dithizone (diphenylthiocarbazone) in 100 ml. of chloroform (analytical reagent quality) and extract with three 25-ml. portions of 5 N hydrochloric acid. Reject the aqueous layers, add 100 ml. of water and 5 ml. of ammonia (sp.gr. 0·880), shake for one minute, allow the layers to separate, reject the chloroform layer and wash the aqueous layer with three further separate portions of chloroform. Add 100 ml. of chloroform, acidify the aqueous liquid with hydrochloric acid, shake vigorously, allow the layers to separate, and draw off the chloroform solution and wash it repeatedly with water until the washings are neutral in reaction; this washed chloroform solution constitutes the purified dithizone reagent and should be kept in a stoppered amber bottle.

The sodium quinaldinate solution is prepared by adding 0·2 g. of quinaldinic acid to 3 ml. of water containing 1 drop of phenolphthalein indicator solution, neutralising with $N/10$ sodium hydroxide solution, and finally diluting to 10 ml. with water. This reagent will remain in good condition for two days if stored in a stoppered bottle.

Resorcinol is employed as a 10 per cent. w/v solution in ethyl alcohol (95 per cent.).

Glacial acetic acid, as used in the actual colour test, should contain not less than 99·5 per cent. of hydrogen acetate.

Procedure.—The preliminary treatment will vary according to the nature of the material to be tested. The procedure is described below in its most comprehensive form, applicable to the examination of organic material containing both zinc and a trace of heavy metals:

Incinerate a suitable quantity of the sample to be tested, containing preferably between 20 and 100γ of zinc, in a silica dish, using a muffle furnace at 500 to 550° C., and extract the carbon-free ash by boiling with a little 10 N hydrochloric acid, and then diluting with water and boiling again. Allow the liquid to cool, dilute to about 100 ml., or other convenient volume, add 0·2 g. of tartaric acid for each 100 ml. of liquid; when this has dissolved, transfer the solution to a separating funnel, add 1 ml. of a 10 per cent. alcoholic solution of resorcinol for each 100 ml. and a few drops of thymol blue indicator solution and then sufficient 5 *N* ammonia to render the colour of the mixture slate blue (approximately *p*H 9). Shake with three successive 10-ml. portions of the purified chloroform solution of dithizone, and transfer the chloroform layers to a second separating funnel; if the third dithizone extract is red or purple, continue the extraction with further portions of the reagent until the chloroform layer remains green. Wash the combined extracts once with 10 ml. of water, run the chloroform solution into a third separating funnel, and shake with four separate 10-ml. portions of *N*/10 hydrochloric acid. Combine the acid layers and wash them free from any mechanically suspended dithizone reagent by pouring small quantities of chloroform through the aqueous liquid without shaking; reject the chloroform used for washing and dilute the acid extract to a convenient known volume with *N*/10 hydrochloric acid. Test a portion of this solution for heavy metals with hydrogen sulphide; if no reaction is obtained, transfer an aliquot part of the solution to a beaker, omit the separation of the heavy metals, and proceed to the determination of zinc, beginning with the evaporation of the acid solution to dryness.

If the slightest trace of heavy metal is present, add to an aliquot part of the solution 1 ml. of a 1 per cent. aqueous solution of cupric chloride for each 50 ml. of solution taken. Boil to remove dissolved chloroform, allow the liquid to cool, add an equal volume of acetone, heat to boiling, and pass in hydrogen sulphide gas until the precipitated sulphides have coagulated. Filter the liquid slowly with the aid of suction through a Gooch crucible previously packed with paper pulp,* and wash with hydrogen sulphide water. Heavy metals having thus been removed, evaporate the filtrate (or if heavy metals were not present originally, evaporate an aliquot part of the original *N*/10 hydrochloric acid extract) to dryness in a beaker of Pyrex glass by gently boiling it over wire gauze. Add to the residue 0·5 ml. of nitric acid and about 5 mg. of potassium chlorate, evaporate to dryness, moisten the residue with a little nitric acid a second time, again evaporate to dryness, and then add a few drops of 5 *N* ammonia and repeat the evaporation. Add to the residue 1 ml. of *N*/2 acetic acid and immerse the beaker in a water-bath adjusted to 60° C. When the residue has dissolved, add 0·5 ml. of sodium quinaldinate solution, *drop by drop*, and continue to warm the mixture at 60° C. for 5 minutes†; then completely transfer the liquid, together with the precipitate of zinc quinaldinate, to a centrifuge tube of 15 ml. capacity, using warm water. Centrifuge, reject the supernatant liquor, wash the precipitate with acetone, and decant the solvent from the precipitate after centrifuging; repeat the washing with acetone twice, and then dry the residue in an oven adjusted to 100° C.

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* *Preparation of Gooch Crucible.*—About 0·2 g. of Whatman No. 1, or similar filter-paper is covered with 10 *N* hydrochloric acid and rubbed with a glass rod until thoroughly disintegrated. After dilution with water, the mixture is poured into a Gooch crucible having a base of about 2 cm. in diameter, and the pulp is gently but firmly packed by pressing it with the flattened end of a glass rod and washed with water until free from acid, suction being used.

† If it is preferred to complete the determination gravimetrically, the supernatant liquid should be drawn off by suction through a filter-stick, the precipitate washed with several portions of hot water, and the beaker and filter-stick dried for about 10 minutes at 125° C. in a current of air in a Benedetti-Pichler drier and finally weighed. The compound has the composition $(C_{10}H_6NO_2)_2Zn.H_2O$ and contains 15·29 per cent. of zinc.

Introduce into a dry Pyrex round-bottomed flask of 50 ml. capacity, fitted by means of a ground-glass joint with an air-condenser, 1 g. of phthalic anhydride, 1·5 g. of naphthalene (recryst.) and 0·5 g. of zinc filings (analytical reagent quality). Introduce 2 ml. of glacial acetic acid into the centrifuge tube, gently boil until the zinc quinaldinate has dissolved, transfer the solution with the aid of a thin glass rod to the Pyrex flask, and wash the tube with three separate 1-ml. portions of glacial acetic acid. Attach the condenser to the flask and gently boil the contents for exactly 20 minutes. Decant the partly cooled solution into a 25-ml. stoppered measuring cylinder, wash the flask several times with a mixed solvent consisting of equal volumes of acetone and ethyl alcohol (95 per cent.), add the washings to the contents of the cylinder and, after cooling, adjust the volume of the liquid to 25 ml. with the same mixed solvent. Transfer a portion of this clear yellow liquid to a 2-inch all-glass cell, and measure the intensity of the colour by means of a Lovibond tintometer. Considering only the yellow component, read the amount of zinc from a curve based on the relationship shown below. Make a control determination to correct for minute traces of zinc present as impurity in the reagents employed, refer the yellow component of the colour obtained to the amount of zinc as shown on the same curve, and deduct the result from that obtained in the primary determination.

Zinc present in the actual test γ	Colour of liquids observed in 2-inch cell Lovibond units		
	Yellow	Red	Brightness
nil	nil	—	—
10	0·9	0·1	—
20	1·8	0·2	—
30	2·7	0·4	0·1
40	3·5	0·6	0·1
50	4·3	0·8	0·1
60	4·9	0·9	0·1
70	5·4	1·0	0·1

If the yellow component of the colour due to the sample is more than 5·4 Lovibond units when measured in a 2-inch cell, repeat the precipitation and colour test, employing a smaller aliquot part of the reserved portion of the hydrochloric acid extract.

Zinc in Natural Waters.—Acidify a suitable quantity (250 or 500 ml.) with hydrochloric acid, using 1 ml. of 10 *N* acid for each 100 ml. of water, boil for 5 minutes, allow to cool, and add 0·2 g. of tartaric acid and 1 ml. of a 10 per cent. alcoholic solution of resorcinol for each 100 ml. of sample taken. When solution is complete transfer to a separating funnel, adjust to *p*H 9 with 5 *N* ammonia and proceed as described above, beginning with the extraction of the zinc with dithizone.

NOTES ON THE METHOD.—The naphthalene used in the colour test acts as a solvent and prevents the excess of phthalic anhydride from crystallising out of solution as the mixture cools. A large proportion of this reagent was found to be essential to obtain full production of the colour.

In calculating the results from the colorimetric observations, only the yellow component is considered, but, as a guide to accurate matching, the data quoted above include the proportion of red tint and brightness, which was found necessary to effect colour agreement.

Of the more commonly occurring metals, only nickel and cobalt interfere. A relatively large quantity of manganese, even if not removed, has no influence on the precipitation of zinc by quinaldinic acid. No interference has been experienced through the presence of phosphates or any other commonly occurring anions.

RESULTS.—The efficacy of the method was first tested by adding known amounts of standard zinc sulphate solution to 50 ml. of water (analytical reagent quality) and submitting the solutions to the complete process of extraction, precipitation and colour test; the results obtained are shown in Table I.

TABLE I

Zinc added, γ ..	70, 85, 35, 50, 75, 10
Zinc found, γ ..	65, 83, 31, 52, 74, 11

Further experiments were made in which small quantities of zinc were recovered from mixtures containing relatively large proportions of heavy metals, iron, phosphates and other salts. In each instance the materials were initially dissolved in about 50 ml. of water (analytical reagent quality). The results are given in Table II. In all these experiments the colours were matched by independent observers having no knowledge of the anticipated values.

TABLE II

Lead added	Iron added	Other substances added	Zinc added	Zinc found
γ	γ		γ	γ
—	500		60	54
—	—	Copper, 500γ	45	46
20	1000		40	31
—	1000		35	36
1000	1000		70	65
200	200	Sodium chloride, 0·5 g. Potassium chloride, 0·1 g. Magnesium sulphate, 0·1 g.	50	44
—	500		50	52
500	500	Mercury, 200γ	80	88
500	500		40	49
—	—	Manganese, 30γ	30	30
—	—	Manganese, 300γ	30	28
500	500		25	25
200	—	Sodium chloride, 0·5 g. Potassium chloride, 0·1 g. Magnesium sulphate, 0·1 g.	80	81
—	—	Sodium phosphate, 1 g.	40	35

The results of a few determinations of the zinc-contents, mainly of foodstuffs and fresh glands, are collected in Table III. The sample of tomatoes was derived from fruit grown under observation in a private greenhouse, and the risk of accidental contamination with zinc from galvanised iron wire, or other source, was eliminated. Of particular interest is the confirmation of an observation already recorded by Sylvester and Hughes[4] that, whereas a sample of egg-yolk was found to contain 26 parts per million of zinc, none was detected in the white. The sea-water was collected in bottles lined with paraffin wax, risk of the sample becoming contaminated with zinc derived from the glass being thus eliminated.

TABLE III

Product	Zinc found p.p.m.
Red Currants	1·2
English tomatoes	4·3
New-laid egg (yolk)	26·0
New-laid egg (white)	nil
Pancreas	13·6
Thyroid gland	10·9
Anterior pituitary gland	20·6
Ditto	29·7
Posterior pituitary gland	12·5
Tap water from London mains	0·23
Sea water collected off N. coast of Cornwall	0·06

SUMMARY.—The extraction of traces of zinc from aqueous liquids with a chloroform solution of dithizone has been investigated, and the process has been made quantitative by the use of resorcinol.

Conditions for separating traces of zinc from relatively large proportions of heavy metals have been studied, and a method for effecting the removal of the latter as sulphides without loss of zinc by adsorption is suggested.

A colorimetric test for the determination of the isolated zinc is proposed.

The method provides a means for accurately determining minute traces of zinc present in biological tissues, foodstuffs and natural waters.

The sensitivity of the colour test is such that determinations of zinc can be conducted on small samples, while in the examination of natural waters the preliminary evaporation of large volumes is obviated.

Nickel and cobalt are the only commonly occurring metals which interfere with the proposed method for determining zinc.

We are indebted to the Directors of The British Drug Houses, Ltd., for permission to publish the results of this investigation.

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LONDON, N.1

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Discussion

Mr. D. D. **Moir** asked if the final reaction liquid, after having been refluxed in the presence of metallic zinc, could be easily separated from the metal in a condition suitable for observation of its colour intensity.

Mr. A. L. **Bacharach** asked if the authors were satisfied that in their process nothing but zinc could be precipitated by the quinaldinic acid.

Mr. J. R. **Nicholls** wished to know if any trouble had been encountered as a result of zinc being extracted from glass-ware.

Dr. B. S. **Evans** also remarked that he had often encountered difficulties arising from zinc present in glass-ware; this was very liable to be extracted by boiling alkaline solutions. Had the authors had any experience with the separation of zinc from cadmium? He, himself, had not been able to separate small quantities of zinc from large quantities of cadmium; in his experience attempts to remove the latter as sulphide resulted in heavy loss of zinc by adsorption.

Mr. **Moon**, replying, explained that the zinc used to promote the colour reaction was in the form of filings and that the supernatant liquid could be readily poured off in a perfectly clear condition. As to the possibility of other metals besides zinc being precipitated by the quinaldinic acid, nickel and cobalt were the only ones of common occurrence which could interfere, since the method provided for the removal of all others which formed insoluble quinaldinates. As regards zinc contamination by glass-ware, trouble had been experienced, but Pyrex glass appeared to be satisfactory. In the method described, the boiling of alkaline liquids in glass vessels was avoided. The authors had not paid any special attention to the question of separating the zinc from relatively large quantities of cadmium, as it was not anticipated that this problem would arise in the examination of biological tissues or natural waters.

Dr. J. H. **Hamence** remarked that he was sorry to hear that the authors had not found the oxine method suitable for their purpose; he rather favoured that reagent for the determination of zinc when present in traces. Had the authors ever found discrepancies in the Lovibond readings made by different observers?

Mr. R. W. **Sutton** said that in his laboratories they had studied the application of the nephelometer to the determination of traces of zinc by means of the ferrocyanide reaction, and had found that they could get accurate results provided that every operation was carefully standardised. It seemed that this might be a suitable method for determining zinc in cadmium. He was surprised to find the authors advocating the removal of other metals by means of hydrogen sulphide; he, himself, had never been satisfied that this time-honoured procedure really did provide a satisfactory separation for zinc but, presumably, the authors' use of acetone overcame adsorption difficulties. He recalled a paper published in Germany about two years ago which prescribed conditions for the successive determination of copper, lead and zinc; in this method the first metal was extracted with dithizone from an acid aqueous solution of the sample, the lead was then removed after neutralisation of the filtrate and addition of potassium cyanide and, finally, the zinc was extracted from the same aqueous liquid after it had been boiled with excess of mineral acid to remove cyanide and the reaction adjusted with sodium acetate.

Mr. **Allport**, in reply, emphasised the point that quinaldinic acid was an exceptionally good precipitating reagent for zinc and, in this respect, was better than oxine; hence it was possible to deal with very small quantities of zinc (for example, 5 to 10μ) without risk of loss. As regards colour measurement by means of the Lovibond tintometer much depended upon the correct adjustment of the brightness and the limitation of the tints to low denominations. Values for brightness, as well as for the red component observed to accompany the yellow tints, were included in the paper as guides to correct colour matching. In all experiments the colours were matched by independent observers having no knowledge of the anticipated results, and in this way the risk of personal bias was eliminated. With regard to the ferrocyanide method the necessity for making a series of standards for every determination constituted a serious disadvantage, even presuming the actual turbidities could be accurately observed. The German method to which Mr. Sutton alluded was that of Strohecker, Riffart and Haberstock (*Z. Unters. Lebensm.*, 1937, **74**, 155) and was cited in the present paper. The method had been tried, but the results obtained were not promising. Summarising, Mr. Allport observed that the method they had proposed had been proved suitable for work within the limits defined by the title of the paper, but he could not vouch for its utility in any wider application, as this had not been investigated.

A Rapid Method for the Determination of Traces of Bismuth in Lead

By R. G. ROBINSON, B.Sc., A.I.C.

THE sharp separation of very small amounts (about 0·001 per cent.) of bismuth in lead is a matter of some difficulty, mainly because lead sulphate persistently retains bismuth.

The ingenious method of internal electrolysis used by Collin[1] would appear to be applicable with difficulty to concentrations of this order.

B. S. Evans,[2] by separating the maximum amount of lead as chloride, minimises the retention of bismuth, but it is the writer's experience that this is by no means negligible when a sulphuric acid solution, containing lead, even in small amount, is heated to the fuming point. As an illustration of this, 3 ml. of a solution containing 0·30 mg. of bismuth as sulphate, 2 ml. of a solution containing 20 mg. of lead as nitrate, and 20 ml. of dilute (1 : 1) sulphuric acid were mixed and heated on the hot plate until the acid fumed, a control experiment without lead being made simultaneously. As soon as fuming of the acid occurred, the beakers were allowed to cool, and 60 ml. of water were added to each. The solutions were gently boiled for 5 minutes, cooled and filtered, and the bismuth was determined by the colorimetric method to be described below. Comparison of the two experiments showed that the lead present in the first had caused a loss of 0·10 mg. of bismuth.

In devising the following method it was desired to avoid this possible source of error, and also to reduce the time by dispensing with any process of evaporation. The scheme finally adopted comprises the following features:

(1) Solution of a 20-g. sample in dilute nitric acid, followed by separation of the major part of the lead as chloride. (2) Co-precipitation of the bismuth with a small amount of ferric iron precipitated as hydroxide. (3) Colorimetric determination of the bismuth as iodide by use of a Lovibond Tintometer. The colour can be measured by means of the yellow units alone.

Attention was first given to the colorimetric determination proper. The presence of ferric iron necessitated the use of an effective reducing agent, but sulphur dioxide, commonly used for this purpose, has serious disadvantages. A moderate excess produces a yellow colour which has been stated to be due to iodine (*cf.* Kruisheer[3]). This assumption seems to be ill-founded, since the yellow substance does not react with starch, and it may easily be confused with bismuth iodide, with which it is identical in colour. After many trials, hypophosphorous acid was found to be a suitable reagent, and it is interesting to note that Fitter,[4] whose priority must be acknowledged, agrees with Nickolls[5] as to the inconvenience of sulphur dioxide and uses hypophosphites in a method for the determination of bismuth in copper.

Hypophosphorous acid is conveniently obtained as a solution (sp.gr. 1·135), and it is to this solution that subsequent reference is made. The reducing action depends largely on the acidity and temperature of the solution, but, in all the trials made, it was found sufficient to warm the liquid to about 70° C. to effect rapid reduction of iodine.

It was found that the bismuth iodide colour reaction was moderately tolerant to variation in acidity, temperature, and iodide concentration, and after consideration of the effect of antimony on the determination, the following conditions were adopted as standard.

The solution, containing 5 ml. of (1 : 1) sulphuric acid, 5 ml. of hypophosphorous acid, and 3 g. of tartaric acid in 100 ml., was poured on to 1·5 g. of solid potassium iodide. After the iodide had dissolved the solution was warmed to 70° C. and then cooled to 20° C., and the colour was measured in daylight in a 1-in. cell. The calibration values given below were obtained with bismuth added as a dilute sulphuric acid solution containing 0·0001 g. of bismuth per ml.

Bismuth added, mg. ..	0·10	0·20	0·25	0·30	0·35	0·40
Yellow units (Lovibond) ..	0·7	1·4	1·7	2·1	2·5	2·9

These values show that the relationship is linear within the limits of error of this method of determining colour, 1 unit of yellow representing 0·143 mg. of bismuth. In using the tintometer it was noticed that yellow is not the easiest of the primary colours to match, and in consequence it was important to avoid optical fatigue. Whenever possible, estimations were checked by another observer without knowledge of the amount of bismuth present, and these values seldom deviated by more than 0·1 unit yellow. The figures given above are taken from a large number of observations which, for the sake of brevity, are not quoted. As noted by Fitter, the colour is very stable, and solutions were exposed to the laboratory atmosphere for 24 hours without change in colour.

As regards the conditions for the colorimetric assay, it was found that, to avoid interference by antimony, it was important to have not more than 5 ml. of dilute (1 : 1) sulphuric acid. If, for example, 20 ml. of the dilute acid were used, and the sample to be assayed contained about 0·25 per cent. of antimony, an indefinite increase in colour of up to 10 units yellow over that expected from the known bismuth-content was observed. This colour was proved to be due to antimony. It faded completely on dilution, and also if the solution was heated to the boiling-point, although it partly returned on cooling. Experiments in which antimony alone was present showed that if only 5 ml. of dilute (1 : 1) sulphuric acid were present, no colour was formed, and it was subsequently proved that under these conditions 5 mg. of antimony caused no interference with the determination of bismuth. When the sample contains an appreciable amount of antimony, tartaric acid is necessary if perfect extraction of bismuth from the ferric hydroxide precipitate is to be effected.

The separation of bismuth together with ferric hydroxide was investigated in tests on a series of solutions containing 0·3 mg. of bismuth, 5 mg. of ferric iron, and 100 mg. of lead, in a mixture of 30 ml. of hydrochloric acid and 130 ml. of water. When iron was precipitated with ammonia in the normal manner, and the precipitate was extracted with a warm sulphuric and tartaric acid solution, approximately only two-thirds of the bismuth present was obtained, the ferric hydroxide precipitate contained much lead, and the filtrate deposited lead hydroxide on cooling. When, however, the solution was free from lead, the bismuth added was quantitatively recovered. Attempts to improve the recovery in presence of lead invariably failed if ammonia was used, but after many trials it was found that a successful separation could be obtained by neutralising carefully to a given point with sodium hydroxide, and, further, that the necessary conditions were rendered less critical by use of an ammonium acetate buffer. Ferric hydroxide thus precipitated carried down only small amounts of lead, and there was no precipitation of lead hydroxide if the solution was cooled. It was not found necessary to digest the precipitate, and in practice it was usually filtered off immediately after precipitation. The maximum amount of bismuth tested was 0·4 mg., and 5 mg. of ferric iron proved sufficient to collect this amount. Antimony, present to the extent of 50 mg., had no ill-effect on the recovery of the bismuth.

THE COMPLETE METHOD.—The lead sample was rolled to a thin tape, and 20 g. were weighed into a 400-ml. beaker and treated with 50 ml. of water and 25 ml. of nitric acid. The beaker was covered and placed on the water-bath until the sample had dissolved. Hydrochloric acid (30 ml.) was then added to precipitate the lead, the contents of the beaker were mixed, cooled to 20° C. or lower, and filtered with the aid of suction through a plug of cotton-wool into a small Buchner flask, and the beaker and precipitate were washed three times with cold (1 : 1) hydrochloric acid. The filtrate was returned to the beaker, which had been washed free from adhering lead chloride, and 5 ml. of a solution containing 1 mg. of ferric iron per ml., followed by 20 ml. of 20 per cent. ammonium acetate solution were added. Sodium hydroxide pellets were then gradually added, while the solution was stirred, until a small amount of lead hydroxide was precipitated. (*Note.*—As progressive additions of sodium hydroxide are made to such a solution, ferric hydroxide is precipitated while the solution is still faintly acid. Further addition of the alkali causes precipitation of lead hydroxide, which redissolves when the solution becomes strongly alkaline, leaving the ferric hydroxide in an apparently uncontaminated condition. Unfortunately, in all tests in which an attempt was made to use this ferric hydroxide precipitate, the bismuth recovery was poor and variable, being at best equal to two-thirds of the amount added; on the other hand, with the ferric hydroxide formed when the solution was sufficiently acid to prevent a visible precipitate of lead hydroxide there was complete recovery of bismuth in every instance.)

After addition of sodium hydroxide as described, the solution was titrated with strong hydrochloric acid, added dropwise with efficient stirring, until the visible lead hydroxide precipitate had just dissolved. A further addition of 1 ml. of acid was made, the ferric hydroxide precipitate was filtered off immediately on a small asbestos mat with the aid of suction, and the beaker and precipitate were washed three times with cold water, the filtrate being rejected. Tartaric acid (3 g.) was dissolved in the beaker in a mixture of 45 ml. of water with 5 ml. of (1 : 1) sulphuric acid, the solution was warmed to about 80° C. and poured on to the precipitate, and the filtrate was collected in a 250-ml. flask, being allowed to flow through the filter by gravity alone, since if suction were applied too early, a faint precipitate of lead sulphate appeared in the flask. When the extracting solution had passed through, the filter was washed twice with water, with the aid of suction, and discarded. The filtrate was treated with 5 ml. of hypophosphorous acid, diluted to 100 ml. with water, and poured into a dry flask containing 1·5 g. of potassium iodide. The liquid was then heated to about 70° C. and cooled to 20° C., and the colour was measured in daylight in a 1-in. cell.

A series of tests of the method is given in Table I, the materials taken for the determinations being:

(A) 20 g. of bismuth-free lead plus 0·1 g. of lead alloy containing 0·1 per cent. of bismuth.
(B) ,, ,, ,, ,, ,, 0·2 g. ,, ,, ,, ,, ,, ,, ,, ,,
(C) ,, ,, ,, ,, ,, 0·3 g. ,, ,, ,, ,, ,, ,, ,, ,,
(D) ,, ,, ,, ,, ,, 0·4 g. ,, ,, ,, ,, ,, ,, ,, ,,
(E) 20 g. of a works batch sample, containing 0·25 per cent. of Sb, 0·01 per cent. of As, 0·10 per cent. of Cu, and 0·25 per cent. of Ag as the major impurities.
(F) 20 g. of a sample of the same batch after softening and desilverising, the impurities now being 0·01 per cent. of Sb and 0·51 per cent. of Zn.
(G) 20 g. of the same batch at a further stage in the refining process, the impurities being 0·01 per cent. of Sb and 0·01 per cent. of Zn.
(H) 20 g. of the same batch after final refining.

In connection with samples (E) to (H), it is the experience of the lead-refining industry that the refining processes carried out as in this instance do not affect the bismuth-content of the lead.

TABLE I

	Bismuth added Per Cent.	Units, yellow	Bismuth found Per Cent.
(A)	0·0005	0·7	0·0005
(B)	0·0010	1·5	0·0011
(C)	0·0015	2·0	0·0014
(D)	0·0020	2·8	0·0020
(E)	nil	2·1	0·0015
(F)	nil	2·1	0·0015
(G)	nil	2·1	0·0015
(H)	nil	2·1	0·0015

With sample (E), which contained 0·25 per cent. of antimony, some care was needed to recognise the correct point when adjusting the solution for precipitation, but the relatively high copper-content did not interfere in any way with the analysis.

Bismuth-free lead was prepared by partially scorifying lead containing 0·0015 per cent. of bismuth, and reducing the resulting litharge by fusion with sodium cyanide. The reduced metal showed complete absence of bismuth within the limits of the method.

Lead-bismuth alloy containing 0·1 per cent. of bismuth was made from bismuth purchased as pure, diluted in two stages with lead containing 0·0015 per cent. of bismuth.

The standard bismuth solutions used for calibration were prepared from the same sample of pure bismuth, and also from bismuth oxide. Weak sulphuric acid solutions, containing 0·0001 per cent. of bismuth, were simply prepared by dissolving bismuth or bismuth oxide in hot strong sulphuric acid and diluting; these solutions proved quite stable. Unless otherwise stated, all acids mentioned are to be taken as being the usual concentrated acids of analytical reagent quality.

The method has been in use for eighteen months in connection with refined lead. If it is required to determine bismuth in antimonial lead, it is necessary to introduce a preliminary separation, which, incidentally, is useful in connection with the determination of various other impurities. It is hoped to describe this separation at a later date.

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BRITANNIA LEAD CO., LTD.
NORTHFLEET
KENT

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The Action of Light on Wool with particular reference to the Production of Acid. I

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THE action of sunlight and ultra-violet light on wool may be considered from two points of view, *viz.* (1) destruction of wearing properties and alteration of affinity for dyestuffs; (2) the chemical changes that take place.

The first of these, commonly termed "weathering," is due to a combination of agencies including bacterial action[1] and traces of atmospheric ozone.[2] Whittaker[3] appears to have been the first to investigate the chemical changes that occur, and said that weathering is due to de-amination. Fort and Lloyd,[4] on the other hand, found that exposure to light causes an increase in amino groups, and Krais[5] held that neither sunlight nor ultra-violet light has any action on wool. Bergen[6] was the first to observe that exposure of wool to ultra-violet light causes the production of acids, owing to part of the sulphur being oxidised to sulphuric acid. Meunier and Rey[7] found that exposure to light causes increased solubility in water and alkalis and that part of the sulphur is oxidised to sulphurous acid, some of which is changed further to sulphuric acid. Bergen[6] concluded that the presence of acid promoted photo-chemical decomposition, whilst alkalis retarded it. Harris and Smith[8] agreed with this view. Some observers have noted destruction of epithelial scales.

In the experiments here described attention has been directed chiefly to the following points: (1) the destruction of epithelial scales and production of structural damage; (2) increased solubility in water and alkalis; (3) the nature of the acid formed, and the protective action of alkali and acid; (4) the effect of moisture and air.

Purified wool and wool containing known amounts of acid or alkali were exposed to the action of both ultra-violet light and light from a Fadeometer. The samples were spread out in thin layers and turned frequently (every hour). The time of exposure was 24 and 48 hours for ultra-violet and Fadeometer light respectively. The wool used was either Botany tops or Botany web. The results differed somewhat with the two kinds owing to the greater surface of the tops, and ultra-violet light produced a greater effect than Fadeometer light.

EXPERIMENTS WITH NEUTRAL WOOL.—The wool was purified by the oleic acid method[9] and gave no reaction for acid or alkali. Hydrogen sulphide was given off during exposure, and a yellowish tint was produced. The exposed wool showed incipient damage of the epithelial scales and occasional fibres in which they had been destroyed. An increased affinity for Kiton Red and diazotised sulphanilic acid, indicating structural damage, was noted. These tests, however, do not establish de-amination. The sulphur was determined before and after exposure, a loss of 0·25 per cent. being found. The exposed wool wetted quickly in water and sodium hydroxide solution. After the wool had been for 12 hours in contact with water and with 0·1 *N* sodium hydroxide solution the losses in weight shown in Table I were recorded.

TABLE I

	Loss before exposure Per Cent.	Loss after exposure Per Cent.
Water	0·16	0·74
0·1 *N* NaOH	1·80	4·80

After exposure to both ultra-violet light and Fadeometer light the wool was strongly acid to methyl red and methyl orange, and this acidity was proved by extraction with alcohol to be due to sulphuric acid. No sulphurous acid could be detected.

The actual increase in acidity is shown in Table II.

TABLE II

	Acid before exposure Per Cent.	Acid after exposure Per Cent.
Tops	0·0	1·13; 1·12
Web	0·0	0·54

A sample of web treated with a very dilute solution of copper sulphate gave 0·98 per cent. of acid. The acidity throughout these experiments was determined both by distillation and by extraction with pyridine. The results agreed as a rule although there were occasional differences, due probably to uneven distribution of the acid.

A weighed quantity of the purified wool was dried in a silica flask and exposed, after the flask had been closed with a rubber bung, to ultra-violet light. The acidity after exposure was 0·74 per cent., indicating that the absence of moisture did not affect the production of acid. When the purified wool was exposed in a silica flask from which the oxygen had been removed no acid was formed but only hydrogen sulphide. It seems that the primary action of light is to break down the sulphur linkages, with production of hydrogen sulphide which, in presence of air, becomes partly oxidised to sulphuric acid. When some pure wool treated with potassium iodide and starch was exposed to ultra-violet light a bluish colour was quickly produced. It is probable therefore that ozone formed at the surface of the wool is the actual oxidising agent. It was shown by Trotman and Langsdale[1] that ozonised air produced some of the characteristics of "weathering," but the production of acid was not investigated.

THE RATE OF INCREASE IN ACIDITY.—Weighed portions of neutral web were exposed to the action of ultra-violet light for varying periods and analysed. The results are given in Table III.

TABLE III

Hours exposed	Acid Per Cent.	Increase
12	0·34	—
24	0·44	0·10
36	0·64	0·20
48	0·74	0·10
72	1·02	0·28

ALKALINE WOOL.—Wool tops containing 0·38 per cent. of alkali as sodium carbonate and alkaline to phenolphthalein was exposed to the action of ultra-violet light for 24 hours.

After exposure it was acid to phenolphthalein but alkaline to phenol red. No damage could be detected microscopically, but faint indications were given with diazotised sulphanilic acid and Kiton Red. The colour was slightly yellow and the wool wetted quickly in water and alkalis. The results of analyses are given in Table IV.

TABLE IV

	Before exposure	After exposure
Alkali, per cent.	0·38	0·05
Sulphur, per cent.	2·99	2·99
Solubility in water, per cent. ..	1·04	1·40
Solubility in *N* NaOH, per cent.	2·24	3·02

Another sample of web containing only a little alkali (*p*H 7·5) gave after exposure 0·29 per cent. of acid. It appears that the acid formed is neutralised by the alkali, and that the presence of the latter exercises a protective action.

ACID WOOL.—Experiments were made with woollen web containing known amounts of sulphuric acid. In every instance the percentage of acid was increased by exposure (Table V). Hydrogen sulphide, but no sulphur dioxide, was given off during exposure. The loss of sulphur was determined in one experiment, and found to be 0·19 per cent. No damage could be detected microscopically. The exposed wool wetted rapidly in water and alkalis and gave faint reactions with Kiton Red and diazotised sulphanilic acid. The solubility in water was nearly the same as that of the alkaline wool (*viz.* 1·20 per cent.), but the solubility in $N/10$ sodium hydroxide solution increased to 6·2 per cent.

TABLE V

Acid before exposure Per Cent.	Acid after exposure Per Cent.	Increase
0·39	0·69	0·30
*0·41	0·74	0·33
0·74	1·23	0·49
1·17	1·72	0·55
1·49	1·99	0·50
2·05	2·64	0·59
5·88	6·35	0·47

* This sample was exposed to the Fadeometer for 48 hours. A second sample treated with a little copper sulphate gave after exposure 1·47 per cent. of acid.

DYED SAMPLES.—Samples of web were dyed in the usual way with an acid dyestuff in presence of Glauber's salt and sulphuric acid; they were then washed and dried. The acidity was determined on weighed portions before and after exposure to ultra-violet light. The results are given in Table VI.

TABLE VI

Dyestuff	Acid before exposure Per Cent.	Acid after exposure Per Cent.	Increase
Bordeaux B	1·76	2·17	0·41
Orange II	2·13	2·50	0·37
Diphenyl chlorine yellow FF (thiazol dyestuff)	2·25	2·65	0·40

SUMMARY.—The conclusions that may be drawn from these experiments are:

(1) Ultra-violet light causes some modification of the wool protein, which increases its solubility in alkalis, and, to a smaller extent, in water.

(2) Neutral wool is more susceptible to the action of light than either acid or alkaline wool, and acid wool is more susceptible than alkaline wool.

(3) The principal chemical change that takes place is liberation of hydrogen sulphide, part of which is oxidised by contact with air (or traces of ozone) to sulphuric acid.

(4) This sulphuric acid is of importance in connection with the determination of acid in woollen goods.

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1, REGENT STREET
NOTTINGHAM
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Generator for "Air-free" Carbon Dioxide (or Hydrogen)

BY S. HORWOOD TUCKER, M.A., D.Sc., A.R.C.Sc., F.I.C.

THE object in designing the generator here described was to obtain a supply of carbon dioxide of sufficient purity to be used for the micro-determination of nitrogen in organic compounds.

"AIR-FREE" CARBON DIOXIDE FOR NITROGEN DETERMINATION.—*Historical.*[1,2]—The Dumas method of determining nitrogen in organic compounds has undergone very little change since it was first introduced. In 1831 Dumas,[3] while attempting to improve Liebig's method, suggested that in making a *qualitative* test for nitrogen it might be removed from the combustion tube by means of carbon dioxide. In 1833[4] he adopted what is essentially the method still in use, *viz.* lead carbonate placed in the closed end of the tube was heated to generate carbon dioxide, which effected removal of air. After combustion of the substance the nitrogen produced was swept out, by renewed heating of the carbonate, and collected over potassium hydroxide solution. Since that time, except for the introduction of Schiff's azotometer,[5] the chief modifications in the method have been concerned with the carbon dioxide supply.

Thus, carbon dioxide has been produced (*a*) by heating the following substances in the closed end of the tube or in a separate tube: carbonates of lead, copper (Liebig, 1837), manganese (Simpson, 1853) and magnesium (magnesite), and the bicarbonates of potassium (Henry and Plisson) and sodium (Melsens, Erdman and Marchant, 1846; Breuer, 1937[6]); (*b*) by the action, in a separate apparatus, of acids on carbonates, *e.g.* chalk + sulphuric acid solution (Hoogewerff and van Dorp, 1882[7]) fused sodium carbonate (also a fused mixture of sodium and potassium carbonates) + sulphuric acid solution (Kreusler, 1885[8]), marble + hydrochloric acid solution (Hufschmidt, 1885[9]), conc. potassium carbonate solution + sulphuric acid solution (Blau, 1892[10]; Young and Caudwell, 1907[11]), potassium bicarbonate solution + sulphuric acid solution (Farmer, 1920[12]; Poth, 1930[13], Lowe and Gutmann, 1932,[14] Reihlen, 1939[15]); (*c*) from liquid carbon dioxide (Ludwig, 1880[16]) and from solid carbon dioxide (Hershberg and Wellwood, 1937[17]).

One of the most convenient methods of preparing carbon dioxide is from marble and hydrochloric acid. For this purpose Kipp's apparatus has been universally used; many modifications of it have been suggested, *e.g.* by Kreusler, 1885,[8] p. 227, modernised by Schoeller, 1921[36]; Böck and Beaucourt, 1928[18]; Trautz and Niederl, 1931[19]; Berger, 1937.[20] A greatly improved generator was introduced by McCoy.[21] Objection has often been brought against the use of marble on the ground that it may contain occluded air. Accordingly, following the practice of Blau,[10] Young and Caudwell[11] used a conc. solution of potassium carbonate + dilute sulphuric acid (1 : 1 by vol.) in an apparatus modelled on one introduced by Thiele, 1899.[22] This type of apparatus suffered, however, from the serious defect that rubber stoppers were an integral part. (This will be referred to again later.) Poth[13] eliminated this defect by devising an all-glass apparatus, which was later improved in design by Lowe and Gutmann,[14] and by Reihlan.[15] They all used potassium bicarbonate solution + sulphuric acid (1 : 1 by vol.). (See also Bradley and Hale, 1908.[23]) Reihlan, 1939,[15] claimed to have prepared *air-free* CO_2, but covered the claim with the statement "Unter 'völlig luftfrei' wird dabei ein Kohlendioxyd verstanden, dessen Mikrobläschen im Azotometer durch eine etwa sechsfach vergrössernde Lupe bei gewöhnlicher Beleuchtung nicht mehr wahrgenommen werden können."

With respect to the use of marble, various attempts have been made to remove air which it is alleged to contain. Bernthsen[24] subjected it to reduced pressure, but Bradley and Hale[23] stated that occluded gases could not be removed from marble (magnesite and the like) "by subjecting the powdered mineral to the continued action of boiling water or of a vacuum." This was reiterated by Poth[13] and tacitly assumed by Reihlan.[15] Pregl and Roth,[25] however, as late as 1937, still recommended as source of carbon dioxide (for the micro-Dumas determination of nitrogen—for which a high state of purity is necessary) marble + hydrochloric acid, the marble being first etched with dilute hydrochloric acid, boiled in water for 10 minutes, and finally left under reduced pressure.

Since the object of this work was to produce a generator which would provide carbon dioxide sufficiently pure for micro-Dumas determinations, I was concerned with providing a *practically*, rather than a *completely*, air-free supply. I do not believe that the latter has ever been obtained, since even Reihlan[15] admitted that unabsorbed bubbles were discernible in the potash solution used for absorption of the carbon dioxide produced by his apparatus.

The chief defect in my opinion in many types of apparatus lies not in the use of marble but in the necessary use of rubber stoppers and connections. Many have found not only that carbon dioxide can pass through rubber, but that air can diffuse through it, even against pressure (Bradley and Hale[23]). On this ground alone one should question the accuracy of the claim of Young and Caudwell,[11] that their apparatus, set up as described, could consistently produce carbon dioxide containing only 1 part of impurity in 50,000; they do not describe how the small volume (0·1 ml.) of impurity and the large volume (5 litres) of carbon dioxide generated were measured.

If, in the apparatus described below, the ground-glass connections are replaced by vaseline-impregnated rubber stoppers* (Pregl–Roth,[25] p. 26), air leaks in, and after about a week is present in sufficient quantity to vitiate a micro Dumas nitrogen determination; but if the apparatus is in daily use leakage is not detectable.

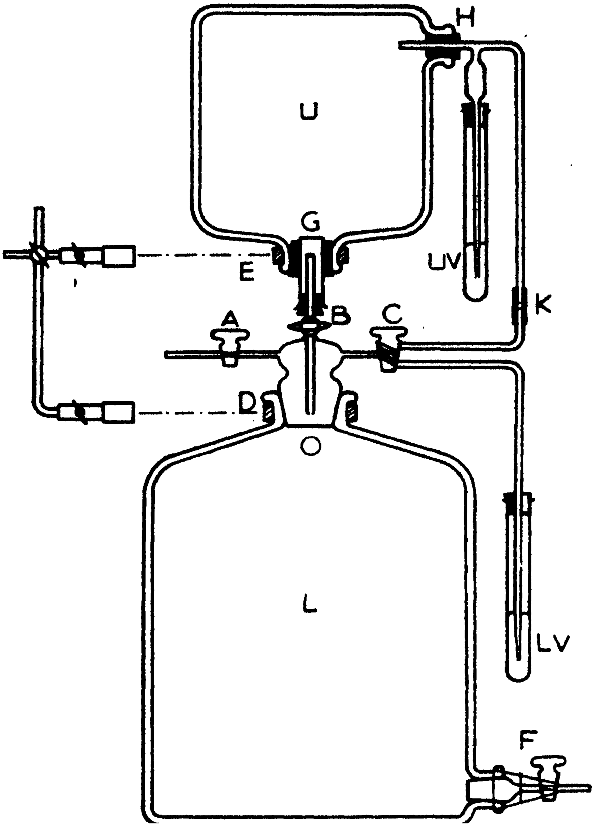

Fig. 1

DESCRIPTION OF "AIR-FREE" CARBON DIOXIDE GENERATOR.—The construction of the apparatus is shown in the diagram (Fig. 1). The lower glass vessel, L, is a Mariotte flask (5 litres) with ground-glass necks into which fit (at F) a glass tap (wired on) and (at D) a ground-glass fitting, ABC,† consisting of two one-way taps, A, B, and one two-way tap, C, the latter enabling connection to be made between the lower vessel, L, and either the upper vessel, U, or the lower mercury valve, LV. The tube to which tap B is attached ends (at O) in a small opening (1 to 1·5 mm. in diameter); it should not be a drawn-out nozzle. The glass fitting, ABC, is attached to the upper, inverted Mariotte flask (U, 2 litres) by rubber stoppers and a glass tube (BG, 5 × 1·2 cm., made by cutting off the closed end of a Pyrex test-tube). The insertion of this tube, BG, enables the upper end of the acid-delivering tube, BO, to remain covered with acid, avoids the use of a rubber connection (between OB and U), and provides a flexible joint which at the same time is firm enough to hold the glass fitting, ABC, down in its socket, D. The upper vessel, U, is supported on the neck of the lower, L, by clamps (at E and D). The upper valve, UV, and the lower, LV, are test-tubes (13 × 1·2 cm.) containing mercury (3·5 cm. deep in UV and 4 cm. in LV). They are attached to the capillary-ended glass tubing by rubber stoppers provided with slit-openings, through which excess carbon dioxide can escape. Water on the surface of the mercury tends to lessen splashing and keeps the mercury clean. The rubber tubing, K, may be of any type, since leakage at this connection is of no consequence.

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* The stoppers were immersed in vaseline contained in a beaker and kept at 80° C. for 10 minutes. The whole was then submitted to evacuation in a vacuum desiccator for about half-an-hour. After atmospheric pressure had been regained the operations were repeated, but evacuation was continued until no more bubbles rose from the stoppers. These were then left to cool under the vaseline at atmospheric pressure.

† Registered (Design No. 833,113) at H.M. Patent Office.

REAGENTS.—Carbon dioxide is generated from marble and hydrochloric acid, which is prepared by mixing the conc. acid with an equal volume of boiled-out water and boiling the mixture for 10 minutes to remove dissolved air. The marble in small chips (1 cm. long) is washed with hot water to remove dirt, and covered with dilute hydrochloric acid (200 ml. of conc. acid diluted with water to fill a Winchester quart). When the effervescence has ceased the liquor is poured away, and the etching process is repeated; but instead of the liquor being poured away, the whole (liquor + marble) is boiled for half-an-hour to remove adherent air and then cooled, this ensuring that the liquor covers the marble.

ASSEMBLY.—All taps and joints should be treated with thick grease, *e.g.* a rubber in vaseline mixture; vaseline by itself is ineffective. The bottom tap (F) is securely wired in—it need never be removed again, even when the apparatus is re-charged. The 5-litre vessel (L) is filled with the marble and covered with the spent liquor in which it was boiled or with boiled-out water. The remainder of the apparatus is fitted up as shown. The upper vessel (U, with B closed) is then filled with the prepared acid, a condenser adapter or funnel + rubber tubing being utilised (at H).

CLEARING OUT AIR.—Taps A and C are closed, F is opened and then B. Acid attacks the marble and the liquor in L is expelled through F; excess of carbon dioxide will escape through the acid in U. (Care must be taken that this evolution is not too violent; if it becomes so, B is closed, A and C (to UV or LV) are opened and F is closed.) L is then evacuated through F by means of the water-pump.* F is closed and B opened. The evacuation is twice repeated. If at any time the pressure (registered by UV) above the acid becomes so reduced that acid ceases to flow through B, pressure may be re-developed by opening C *momentarily* (so as to connect L with U). It is not usually necessary to resort to this expedient, since, normally, bubbling back (through B) is sufficient to maintain the pressure (registered by UV); but in order to remove the last traces of air from the acid (Farmer[13]) the operation described above (opening C momentarily while B is permanently open) should be repeated a number of times. The process further serves to displace air from above the acid (in U) and thus preserve it permanently from re-contamination. C is opened and air is driven from the tube leading to the valve LV. If the apparatus is not yet quite free of air, evacuation may be repeated, or L may be flushed out by closing A and C, and then opening B and F alternately. The generator is left with A and B closed and C open to LV. When necessary spent liquor is removed by closing A and C and manipulating B and F as just described.

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* Although no implosion has ever occurred, it is advisable, as a precautionary measure, to carry out this operation behind the screen of the draught cupboard.

The expedient, adopted by Reihlan,[15] of leaving his apparatus standing full of carbon dioxide for several days to allow air to be displaced from glass surfaces does not seem to be necessary with the generator now described, after the above evacuation.

MANIPULATION.—To obtain a supply of carbon dioxide, close C and open B. Then, since the pressure in L is almost invariably greater than that in U, bubbles of carbon dioxide will escape upwards through B and through the mercury in UV. Pressure will thus be established. If this does not take place, open C (to UV) *momentarily* (*cf.* above). Open A to deliver carbon dioxide. With B fully open the flow of acid is usually so great that a large excess of carbon dioxide is produced (and escapes through UV). Accordingly, B is adjusted so that the bubbling back (intermittent) is only sufficient to maintain the head of mercury in UV. When so set the generator works automatically.

When the supply of carbon dioxide is no longer needed A is closed and the generator may be left with B adjusted as above. No acid will enter L unless B is open too wide, or the temperature of the environment changes considerably. In any event only a wastage of reagents occurs. This is a convenient condition in which to leave the generator when it is in intermittent use; carbon dioxide is then immediately available and controllable by manipulation of tap A only. However, if the generator is left unused for longer than a day it is economical to close B and open C so as to connect L with the valve LV. In this condition it may be left in a perfectly air-tight condition for any length of time; when again required, unimpaired carbon dioxide will be at once obtainable.

TESTING THE GENERATOR.—Carbon dioxide was passed into a micro-azotometer for 3 hours, bubbling being continuous and regular without any adjustments being intermediately required. With 5 bubbles passing per second, 0·010 ml. was collected in 3 hours, *i.e.* 0·0006 ml. in 10 minutes. In the micro Dumas nitrogen determination carbon dioxide is passed at a much slower rate than 5 bubbles per second, and for about 10 minutes only. Hence the above supply would not give the lowest observable amount (0·001 ml.) of unabsorbed gas during the determination.

To gain an *approximate* idea of the volume of carbon dioxide passed in 3 hours, the apparatus was set up as described above, and when the stream into the azotometer was 5 bubbles per second, the potassium hydroxide solution was run off and replaced by water. The carbon dioxide was then collected in an auxiliary receiver; it measured 1045 ml. in 3 hours. Hence 1045 ml. contained 0·010 ml. of unabsorbed gas, *i.e.* less than 1 part of unabsorbed gas in 100,000 parts of carbon dioxide.

ADVANTAGES OF THE GENERATOR.*—(1) A practically air-free supply of carbon dioxide sufficiently pure for micro nitrogen determination is obtainable.

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* The generator (without mercury) may be obtained through the usual retailers, from Messrs. G. W. Flaig & Sons, Ltd., 57, Hatton Garden, London, E.C.1; price £3.

(2) A continuous or discontinuous supply of carbon dioxide at a regular and adjustable pressure is obtainable by manipulation of one tap only.

(3) The total supply of carbon dioxide is limited only by the size of the marble-container; which may be of any desired size without alteration of the small area of ground glass surfaces. With the 5-litre size, several hundred micro-analyses may be carried out from one charge.

(4) There are no rubber connections through which air may enter and vitiate the carbon dioxide.

(5) The generator may be set aside for an indefinite period without wastage of reagents or lowering of quality of the carbon dioxide taking place.

(6) The same generator may be used for the preparation of *air-free hydrogen* from granulated zinc and hydrochloric acid (prepared as described above).

I am indebted to Mr. J. M. L. Cameron of this Department, who has greatly assisted me with suggestions and in testing the apparatus.

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March, 1939

The Volumetric Determination of Organic Picrates and Picrolonates with Methylene Blue

By ADOLPH BOLLIGER

A NUMBER of nitrophenols and organic acids combine with methylene blue to form salts which are only slightly soluble in water but more soluble in chloroform. By applying this property a titration method has been evolved for the micro-determination of suitable nitrophenols and aromatic acids, as well as of their salts and addition compounds.[1,2] Of the nitrophenolates tested, picrates are the most suitable substances for titration with methylene blue, and the rapidity, as well as the accuracy, of this procedure warrants a description of the determination of the organic picrates that are frequently prepared. Picrolonates are also readily determined by this method if certain precautions are taken.

PRINCIPLE.—The picrate is titrated with 0·001 *N* methylene blue solution, and the methylene blue picrate or picrolonate formed in the titration is extracted with chloroform from the aqueous layer. Since methylene blue is practically unextractable with chloroform, it is possible to detect the end-point by the colour of the aqueous layer, the titration liquid acting as indicator.

REAGENT.—Approximately 0·001 *N* methylene blue solution. First, an approximately 0·01 *N* stock solution is prepared by dissolving 3·8 g. of chemically pure methylene blue in water and diluting the solution to 1 litre. (We used methylene blue "Merck, medicinal, chemically pure, free from chloride of zinc, $C_{16}H_{18}N_3SCl + 3H_2O$"); 0·001 *N* methylene blue solution is obtained from the stock solution by dilution. These solutions, when preserved with a few ml. of chloroform and kept in a dark bottle, remain sufficiently stable for several months. The 0·001 *N* solution of methylene blue is standardised against a 0·001 *N* solution of chemically pure picric acid by the titration method described below.

METHOD.—From 1 to 15 mg. of the substance to be titrated is weighed on the micro-balance and used as such, or an aqueous solution containing a known amount of the substance may be prepared. If the substance is not readily soluble in water, sufficient pyridine may be added to bring about complete solution, or the substance may be dissolved in chloroform. The solid substance, or a measured amount of the solution containing approximately 1 to 15 mg., is transferred to a cylindrical separating funnel containing a few ml. of water and about 20 ml. of chloroform. Aqueous methylene blue solution of known strength (approx. 0·001 *N*) is run in from a burette, and the funnel is shaken to extract the methylene blue picrate from the aqueous layer by means of the chloroform already present. The chloroform layer, which separates very rapidly, assumes a green colour, while the yellow colour of the aqueous layer diminishes correspondingly. The titration is continued, the chloroform being renewed when it is saturated with methylene blue picrate or when the aqueous layer has assumed the green tint, although not the intensity of colour, of the chloroform layer. In the latter event, the aqueous layer, after extraction with fresh chloroform, becomes pale yellow. If a pale yellow colour of the aqueous layer has been reached, the methylene blue is added, drop by drop, and the chloroform is frequently renewed. Theoretically, the end-point is reached when the aqueous layer has become completely colourless and when no more methylene blue picrate can be extracted from the aqueous layer. For practical purposes, however, the end-point is not considered to be reached until one drop of methylene blue changes the almost colourless solution to a faint but distinct blue which completely resists further extraction with fresh chloroform.

After a little experience it is easy to recognise the end-point by observing the changes in the aqueous layer, as described. For some observers, it may be somewhat easier to detect the end-point by observing the colour of the chloroform layer. As already mentioned, the yellow colour of the aqueous layer diminishes during the progress of titration, whilst the chloroform layer turns correspondingly deeper green. For the modified method of observing the end-point, the chloroform is renewed after every drop of the methylene blue solution as soon as the end-point is approached. The fresh lots of chloroform have to be of equal volume (for example, 10 ml.), and they are kept separately in a test-tube after each extraction. As long as picric acid is present in the aqueous layer, the chloroform extracts will be distinctly greenish. The end-point is reached when a distinct diminution and alteration of the colour of the extract from greenish towards a very faint blue occurs. This last sample is of the same colour as that obtained in a blank experiment containing about the same amount of water plus one drop of methylene blue solution extracted with a similar amount of chloroform. If, for some reason, the end-point has been overstepped, one can titrate back with 0·001 *N* picric acid solution.

Organic picrolonates are titrated in the same manner. However, one has to consider the fact that picrolonic acid is much less soluble than picric acid and that organic picrolonates frequently are very sparingly soluble. Therefore, it is frequently necessary to dissolve such picrolonates beforehand, in order to avoid losses during the process of titration. This is sometimes best effected by decomposing the sparingly soluble picrolonate in a boiling aqueous solution of lithium carbonate. The lithium salt of picrolonic acid formed is readily soluble. However, no considerable excess of lithium carbonate must be present, otherwise the results obtained will be too high. If an excess of lithium carbonate is present it is necessary, after the solution has been transferred to the separating funnel and immediately before the titration, to acidify slightly with sulphuric acid and to neutralise the excess of sulphuric acid by the addition of calcium carbonate.

The following table gives results obtained by titrating picrates and picrolonates with methylene blue:

	Amount analysed mg.	0·001 *N* methylene blue used ml.	Picric acid	
(*A*) *Picrates.*			Found Per Cent.	Calculated Per Cent.
Nicotine picrate	4·68 (solution)	15·1	73·9	73·9
		15·0	73·4	
Naphthalene picrate	7·770 (solid)	21·6	63·7	64·1
Acenaphthene picrate	8·85 (solution)	23·1	59·7	59·8
		22·9	59·3	

(*B*) *Picrolonates.*	Amount analysed mg.	0·001 *N* methylene blue used ml.	Picrolonic acid Found Per Cent.	Picrolonic acid Calculated Per Cent.
Nicotine picrolonate	4·171 (solution)	12·2	77·2	76·5
p-Bromoaniline picrolonate	11·56 (solid)	26·6	60·8	60·5
		26·8	61·2	
Dibenzylamine picrolonate	9·18 (solution)	20·1	57·7	57·3

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF COPPER

THIS method for the determination of copper in alloys of the Duralumin type was designed primarily to supplement the electrolytic method. It has proved to be much quicker than the latter, while retaining an accuracy well within the limits usually required for general routine work, and it requires no special or expensive apparatus. Indeed, a minimum of apparatus is used, as all the operations are conducted in one and the same beaker.

It is a variation of the iodimetric procedure but involves no separations. Iron and manganese, which interfere quantitatively in the oxidised state, are reduced by excess of sodium sulphite, which excess is destroyed by boiling, and re-oxidation is permanently inhibited by the presence of the excess of aluminium sulphate.

PROCEDURE.—One g. of the drillings is placed in a covered 350-ml. Pyrex conical beaker and dissolved in 35 ml. of the following acid mixture:—water, 6; conc. hydrochloric acid, 3; conc. nitric acid, 3; conc. sulphuric acid, 1·7 vols. The solution, still under cover, is boiled gently for a few minutes and then evaporated rapidly to dryness on the hottest part of a hot plate. The white cake, after cooling somewhat, is covered with about 100 ml. of boiling water, and 5 ml. of a freshly prepared 4 per cent. solution of sodium sulphite hexahydrate is added together with a few mg. of finely powdered quartz. The solution is boiled steadily for 10 to 15 minutes, and then cooled in running water. The cover is rinsed into the beaker, and about 2 g. of solid potassium iodide (measured in a spoon) are added. The solution is shaken to dissolve the reagent and titrated at once with standard sodium thiosulphate solution (1 ml. = 0·0025 g. of Cu), starch solution being used as an indicator. If the titration is conducted at 35–40° C., the end-point is sharp.

The following are typical comparative results obtained by the electrolytic and iodide methods:

Electrolytic Per Cent.	Iodide Per Cent.	Difference
3·95	3·90	0·05
4·33	4·33	nil
4·00	4·02	0·02
4·50	4·50	nil
4·89	4·85	0·04
4·50	4·51	0·01
4·61	4·58	0·03
4·69	4·62	0·07
3·39	3·38	0·01
3·20	3·15	0·05
3·52	3·58	0·06
4·50	4·45	0·05
4·54	4·53	0·01
3·21	3·15	0·06
4·08	4·15	0·07
4·19	4·25	0·06
4·17	4·18	0·01
4·39	4·35	0·04
4·30	4·30	nil

In 53 determinations on samples in which the copper-content ranged from 3·19 to 4·89 per cent. the discrepancies between the results obtained by the two methods were as follows:—In 2, 0·07; in 5, 0·06; in 5, 0·05; in 10, 0·04; in 9, 0·03; in 8, 0·02; in 8, 0·01; in 5, nil.

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SCREENED METHYL ORANGE

The use of xylene cyanol FF to "screen" the colours given with methyl orange indicator was first mentioned by Hickman and Linstead (*J. Chem. Soc.*, 1922, 2502; Abst., Analyst, 1923, **48**, 89) and commented on favourably by A. D. Mitchell in his lecture to the Institute of Chemistry in 1934. A very sharp end-point at *p*H 3·8 could thus be obtained.

On testing a bought sample of screened methyl orange in an ordinary HCl—NaOH titration, I obtained results that were unsatisfactory and showed no advantage over those with unscreened methyl orange, and the end-point was not sharp. On making up some screened methyl orange from solid xylene cyanol FF and solid methyl orange in the proportions given in Hickman and Linstead's original paper, I again obtained similar unsatisfactory results.

I found, however, that by using the same solid methyl orange with solid xylene cyanol FF from another source of supply, the result was entirely satisfactory, and the end-point at *p*H 3·8 was very sharp. Good results were also obtained with the first-mentioned sample of xylene cyanol FF if I used it in about double the proportion per unit of methyl orange, namely, 2·8 g. of xylene cyanol FF, instead of 1·4 g. per 1 g. of methyl orange, in 500 ml. of 50 per cent. alcohol.

It would thus appear that samples of xylene cyanol FF are liable to vary considerably. The poor sample was of a deep indigo colour in the solid state, but when dissolved alone in 50 per cent. alcohol it gave a blue solution paler than that of a solution of the good sample at the same concentration. In the solid state the good sample was greyish-blue.

The poor and good samples of xylene cyanol FF gave the following respective colour changes with screened methyl orange:

*p*H	Poor sample	Good sample
3·1	Red	Purple
3·6	Reddish-brown	Greyish-purple
3·8	Yellow-brown	Grey
4·0	Yellow-brown	Greenish-grey
4·2	Yellow	Green

This note may be of value to analysts, as an indicator giving a sharp end-point at *p*H 3·8 is useful in many titrations.

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A USEFUL AID TO SUGAR ANALYSIS

IN recent years the Lane and Eynon method of sugar determination has won deserved popularity amongst food analysts. From our practical experience, we are of the opinion that once the technique of the method has been thoroughly grasped, and provided that the conditions of carrying out the test are followed exactly, it is possible to obtain a series of successive titrations which do not differ from each other by more than 0·05 ml. When, therefore, it was observed that this order of accuracy was obtainable, it then became necessary to take one of three steps in order to obtain a result in keeping with this standard of accuracy.

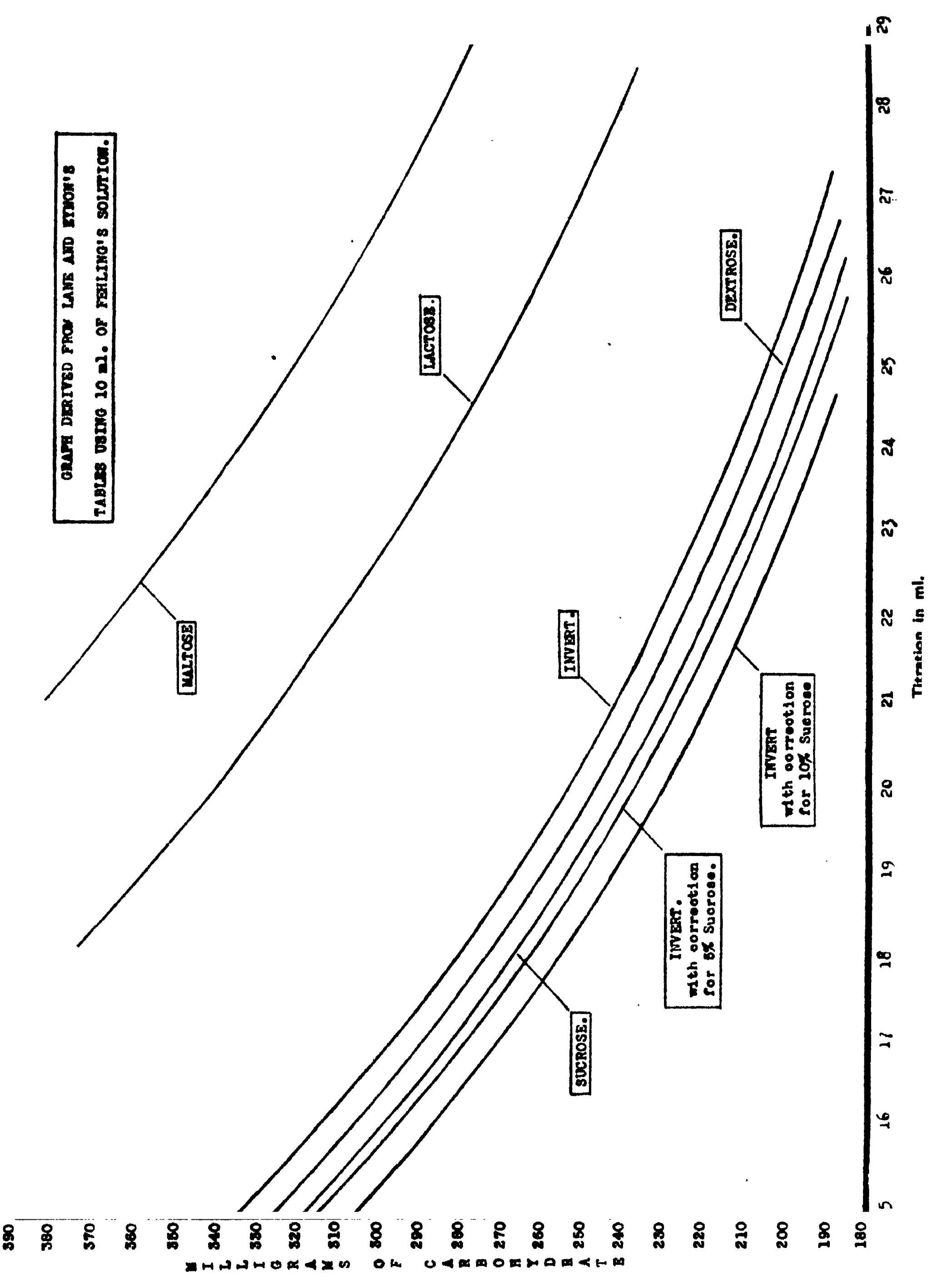
(1) To extend more fully the Lane and Eynon tables, so that readings would be available for every 0·05 ml. between 15 and 50 ml. This would involve the recording of over 700 readings for each particular sugar, and the idea was therefore discarded on the grounds of being impracticable.

(2) To apply the factor that is given in the tables for the nearest whole number of ml. This offers no serious objection, except in so far as the analyst would be continually dealing with a different factor in every calculation.

(3) To prepare a graph by interpolation of the Lane and Eynon tables in such a way that the milligrams of carbohydrate in 100 ml. of solution would be given directly for any particular titration. We formed the opinion that if the idea underlying this last method were investigated, then once the necessary graph had been prepared, a ready means would be available for calculation of all Fehling determinations without the introduction of any troublesome factors.

We outline below a description of the type of graph that we have prepared and have found of considerable use during the past twelve months.

The graph was constructed from the Lane and Eynon tables, by plotting milligrams of carbohydrate per 100 ml. of solution against the results of Fehling titrations for most of the common sugars. The linear dimensions were approximately 25 in. × 19 in. The graph was mounted on a wooden framework provided with a sliding cursor also made of wood. This cursor had a printed titration scale running along the whole of its length, and was so constructed that it could slide in a direction parallel to the longitudinal axis of the graph.


GRAPH DERIVED FROM LANE AND EYNON'S TABLES USING 10 ml. OF FEHLING'S SOLUTION.
MALTOSE
LACTOSE.
DEXTROSE.
INVERT.
INVERT with correction for 10% Sucrose
INVERT. with correction for 5% Sucrose.
SUCROSE.
Titration in ml.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
MILLIGRAMS OF CARBOHYDRATE
180
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390

To use the graph in actual practice, the following procedure is recommended:—Begin by obtaining the Fehling titration by the Lane and Eynon method, and then move the cursor in an upward direction until the figure on the scale attached, corresponding with that obtained by titration, cuts the curve of the particular sugar being determined. Then, if the eye is cast along the cursor to the point where it cuts the vertical axis of the graph, the milligrams of carbohydrate present in 100 ml. of solution may be read directly.

In the accompanying diagram it will be noted that a curve for sucrose is also indicated. This, of course, was prepared by multiplying the invert sugar figures by 0·95. We wish to point out that if the number of sugar determinations carried out in any particular laboratory is sufficiently large to warrant the use of this graph, it would have to be constructed to individual requirements and one or two minor alterations carried out. Thus the graph described above covers only a range of titrations from 15 to 29 ml., although Lane and Eynon have published factors for titration from 15 to 50 ml. Also, we use only 10 ml. of Fehling's solution for titration, but a similar graph can be prepared for use with 25 ml. if required.

We wish to record our thanks to Mr. A. S. Houghton and to Messrs. Fuller's, Ltd., for permission to publish this note.

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MICROBIOLOGY IN THE PRESERVATION OF THE HEN'S EGG*

The Report summarises existing knowledge on the avian egg in general, with special reference to the hen's egg, and discusses the subject under the following divisions:—(1) The anatomy and physiology of the bird and developing ovum, especially in connection with possible microbial activity. (2) The structure and chemistry of the egg in their relation to the micro-flora of the environment. (3) Consideration of factors operating during storage in so far as these are relative to the microbiology of the subject.

Microbiology of the Egg during Ovi-deposition.—For many years the view has been promulgated that, whilst the infertile egg may be bacteriologically sterile, the fertilised egg frequently is not. The general conclusion, drawn from a consideration of the published work, is that it is possible that, although fertilisation apparently does not lead to increased bacterial infection, it may set going a chain of enzymic and physiological changes rendering the fertilised ovum more susceptible to bacterial decomposition, but there appears to be no scientific evidence on this question. Experimental work has shown that the bird displays a high degree of resistance towards bacterial infection and, in particular, that even when the ovary does become infected, the infection is not readily transferred to the egg. The balance of experimental evidence does not support the trade view that infection of the egg increases with the age of the hen.

Microbiology of the Egg after Laying.—The number of "rots" is much higher, as would be expected, with eggs with dirty shells than with clean ones, but washing, or cleaning the shells in any way, is useless and in fact increases the rate of deterioration. The reason for this has apparently not yet been definitely established. It may be that washing removes the coating from a sound egg and thus renders it more susceptible to subsequent bacterial infection, or it may assist the passage of the bacteria already on the shell into the egg. Again, the coating of mucin deposited on the newly-laid egg may itself have a germicidal action. These are points that require further investigation.

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* Food Investigation. Special Report No. 47. By R. B. Haines, D.Sc., Ph.D. Pp. 65. With 3 plates and 5 figures. H.M. Stationery Office, York House, Kingsway, London, W.C.2. March, 1939. Price 2s. 6d. net.

Since the spoilage of eggs is due above all to microbiological activity, it follows on general grounds that all possible steps should be taken to reduce the infection at all points of handling. Hay and straw in general being known to harbour great numbers of micro-organisms, clearly the egg should be kept out of contact with them as far as possible.

There are substances in egg-white which are inimical to bacteria, but, rather surprisingly, the white of really fresh eggs has a weaker germicidal action than that of older eggs. The explanation suggested is that as the egg gets older it loses carbon dioxide and the white thus becomes so alkaline that most organisms cannot grow in it. Moreover, there is a substance in the white of eggs (and also present in human tears), which has the property of "lysing" the organisms by dissolving them. With one variety of bacteria, a dilution of one of egg-white in two millions produces complete lysis of a thick suspension of the organism in three hours at a temperature of 113° F., and a dilution as low as one in sixty millions has a definite effect.

A number of requirements must be fulfilled before the micro-organisms can elaborate the substances, *e.g.* enzymes, which cause deterioration. For example, even the most active organisms require the presence of simple compounds before they can begin to grow, and must synthesise their enzymes before the decomposition of protein can begin. Sown into solutions of purified proteins, they die. Hence the amount of decomposition occurring in eggs before contaminating bacteria have access to them must have a great influence upon the ease with which the organisms grow and effect further decomposition. This, in turn, presumably depends on the rapidity with which the eggs are gathered and cooled to a temperature sufficiently low to minimise enzymic changes.

In the rotting of eggs caused by fungi, when the fungus penetrates as far as the yolk the yolk-membranes may be ruptured, and once this stage is reached, luxuriant growth of the fungus occurs. Rotting takes place rapidly in eggs with "sided yolks," and it is assumed that this is due to infection from the outside of the shell being able to penetrate more or less directly into the yolk, where it flourishes.

MICROBIOLOGY OF THE EGG DURING STORAGE.—The Report describes the commonest deleterious flavours or odours in stored eggs as "mustiness," "fishiness" and "cabbage-water" in the white, and a "strong" flavour in the yolk. The first three of these are micro-biological in origin. The cause of the last is not always clear, but it has been suggested that a "strong" or "storage" taste appearing after about seven months' storage is due to the absorption of odours from the surroundings, especially from straw-board fillers.

Briefly, the methods for reducing the spoilage of eggs by the activity of micro-organisms during storage are as follows:—hygienic production and handling, coupled with strict elimination of all inferior material; preservation of the natural defences of the egg; control of temperature and of humidity, and the use of gases, such as carbon dioxide, or of other means, such as sealing the pores of the eggs, for retarding the growth of the organisms.

Eggs to be cold-stored should be cooled as rapidly as possible to temperatures near 0 °C. This eliminates the possibility of "blood-heat" organisms multiplying, which means that the incidence of the most potent form of black rotting, due to *Proteus* bacteria, will be minimised. However, not only must the egg be rapidly cooled to, and kept near, 0° C., but adequate precautions must also be taken when it comes out of store. *Proteus* bacteria, although partially or completely prevented from developing during storage at 0° C., do not necessarily die under these conditions, and the slow chemical and physical changes occurring during prolonged storage are likely to render the egg all the more easily attacked by surviving rot-producing organisms when the temperature is again brought within the range at which they grow. Ideally, therefore, cold-stored eggs should be used immediately on removal from storage. The high incidence of black rot occasionally found in imported eggs is almost certainly due to the eggs being allowed to stand about at too high a temperature after removal from storage.

The result of work upon the control of humidity to avoid the possibility of fungal spoilage indicates that the humidity of the store should not exceed 80 to 85 per cent. Dealing with other methods for reducing the growth of micro-organisms, the Report states that methods of storage depending on the exclusion of air, which prevent the growth of organisms needing oxygen, have been developed in a variety of ways. In the dry packing of eggs, salt, lime, bran, sawdust, ashes, sand and sulphur have all been used. None of these packings is completely successful in its objectives. Sealing with wax, with aluminium soap, or by immersion in waterglass is much better. The last method works well, eggs having been kept in good condition for several years by storage in waterglass. Its drawback, commercially, is the bulk of the packing material. Before being sealed with wax, the eggs are frequently evacuated, and the wax may be applied hot. Partial sterilisation, with better sealing of the pores, is thus accomplished.

Use of Carbon Dioxide.—The Report gives considerable attention to the use of carbon dioxide in the storage of eggs. Commercial methods for the gas storage of eggs, in which carbon dioxide has been used in conjunction with cold storage, have been developed by the Low Temperature Research Station at Cambridge. These are described in Food Investigation Leaflet No. 8 (The Cold Storage and Gas Storage of Eggs) copies of which are obtainable gratis on application to the Secretary, Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W.1 (*cf.* ANALYST, 1939, 281).

BIBLIOGRAPHY.—The Report concludes with a detailed bibliography of six pages containing 158 references.

U.S.A. Commercial Standards for Disinfectants

THE National Bureau of Standards of the United States Department of Commerce has approved commercial standards for a number of disinfectants. The specified requirements include the following:

LIQUID HYPOCHLORITE DISINFECTANT, DEODORANT AND GERMICIDE.—The available chlorine present must be not less than 2·5 per cent., and the amount shall be clearly stated on the label. The loss in the available chlorine-content shall not exceed 10 per cent. when the disinfectant is stored in a cool, dark place at a temperature not exceeding 20° C. (68° F.). The preparation must be miscible in all proportions with water of zero hardness, and shall be ready for dilution when delivered.

PINE OIL DISINFECTANT.—This shall be the product of pure steam-distilled pine oil (of which it must contain not less than 60 per cent. by weight) mixed with an emulsifying agent. It shall remain clear and homogeneous under normal and reasonable conditions of storage. It must not contain more than 10 per cent. of water. The phenol coefficient, which shall be determined against *B. typhosus* by the Federal Food and Drug Administration method, must be stated on the label. The preparation shall not contain kerosene or other petroleum distillates. When 5 parts are diluted with 95 parts of water of zero hardness at 20° C. it shall form a stable emulsion, which shall show no sign of floating oil after it has stood for at least 24 hours.

COAL TAR DISINFECTANT (EMULSIFYING TYPE).—This shall consist of not less than 65 per cent. by weight of coal tar oils and acids, and an emulsifying agent, and shall not contain more than 10 per cent. of water. It must not contain kerosene or other petroleum distillates. The phenol coefficient, determined against *B. typhosus*, must be stated on the label. The product must form milky emulsions when diluted with water of zero hardness at 20° C. in the ratio of 5 parts of disinfectant to 95 parts of water for disinfectants with a phenol coefficient of 10 or under; or in the ratio of 2 parts of disinfectant to 98 parts of water for disinfectants with a phenol coefficient exceeding 10. These emulsions shall show not more than a trace of floating oil when stored for five hours at room temperature. There must be no sign of naphthalene crystallisation after 12 hours at 0° C. The preparation must contain less than 5 per cent. of benzophenol.

CRESYLIC DISINFECTANTS.—The product shall be made from that portion of coal tar known as "tar acids," and a soap derived from rosin acid and/or fat of vegetable origin. It shall contain not less than 50 per cent. of tar acids, as determined by the U.S.P. XI method for the assay of cresol in the saponated solution of cresol. It shall not contain more than 25 per cent. of inert ingredients (water plus glycerin, if any). The phenol coefficient, as determined against *B. typhosus*, must be stated on the label. It must contain less than 5 per cent. of benzophenol. When mixed with water of zero hardness at 20° C. it must yield a clear solution within the concentration range of 1 to 4 per cent. Such solutions, when kept in close containers, shall remain either practically clear or become only slightly opalescent when allowed to stand for 24 hours at 20° C. away from direct light. When kept at 0° C. for three hours the preparation shall not show any separation of soap.

HOUSEHOLD INSECTICIDE (LIQUID SPRAY TYPE).—The killing power shall be determined by the official Peet-Grady method in conjunction with the official test insecticide of the National Association of Insecticide and Disinfectant Manufacturers, Inc. The product shall have a flash-point not lower than 125° F. when tested in the Tagliabue closed cup.

U.S. Department of Commerce
National Bureau of Standards

MICROSCOPIC METHODS USED IN IDENTIFYING COMMERCIAL FIBRES*

THIS publication is a compilation of methods collected during a survey of the literature of the subject. All have been tried and found useful, and their relative merits are discussed. A bibliography of 48 references is included.

PAPER FIBRES

PREPARATION OF THE SAMPLE.—(1) *Federal Specification Method* (General Specification, UU-P-31, Sect. IV, Pt. 5, March 1, 1932).—A piece, about 5 mm. square, is cut from each of 10 sheets representing the delivery, and the pieces are boiled with 20 ml. of 2 per cent. sodium hydroxide solution and washed well with water. They are then rolled into a ball with the fingers and shaken in a test-tube with water until the fibres are completely separated. About 5 ml. of the suspension is transferred to another test-tube and again shaken with water, and as small a quantity of the fibres as can be taken up with a needle or with forceps is then placed on a microscope slide, and the water is removed by means of absorbent paper.

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* Circular C.423, by T. M. Plitt. Pp. 26. Issued March 14, 1939. Superintendent of Documents, Washington, D.C., price 10 cents.

(2) *T.A.P.P.I. Method* ("Tentative and Official Testing Methods—Recommended Practices—Specifications," *Tech. Ass. of the Pulp and Paper Ind.*, **1936**, T 401, m 36).—This is similar, except that the total area of samples should not be less than 6 sq. cm.; 0·5 per cent. alkali is used, and the fibres are transferred to the slide as a suspension which is subsequently dried in an air-bath; a 200-mesh sieve is used to separate the fibres from the alkali.

(3) *Short Method.*—The sample is boiled for 1 minute in 2·5 per cent. alkali, and the fibres are loosened first with the fingers and subsequently by stirring in an excess of water. A pipette is used to transfer the suspension to the slide, and the excess of water is removed with absorbent paper. In addition to rapidity this method has the advantage compared with (1) and (2) that there is no preferential selection of longer fibres by the needle or mesh, respectively.

QUANTITATIVE ANALYSIS.—(1) *Federal Specification Method.*—The whole of the surface of the prepared slide is systematically scanned under the microscope, at least 300 fibres being counted.

(2) *T.A.P.P.I. Method.*—A magnification of not less than 100 diameters is recommended, and a description is given of the preparation of a cross-line disc from two silk threads, which are cemented to a cover-slip which is fixed centrally under the diaphragm of the eyepiece of the microscope. The fibres are counted at various points in a straight line, twice lengthwise and four times across the slide, each line of observation being started at a different point; at least 25 different fields comprising 600 fibres, on 3 slides, should be counted. The fibres are recorded by counting each fibre as it passes under the intersection of the cross-lines, regardless of its size. Results are reported (as the percentage of the particular fibre present) to the nearest 5 per cent.

STAINS.—(1) *Herzberg General Stain.*—The Federal Specification and Merritt modification are given. For the latter (*Paper Trade J.*, 1922, **75**, 91TS), which is preferred, exactly 25 ml. of water are shaken with 50 g. of dry zinc chloride, and the sp.gr. is adjusted to 1·8 at 28° C. The solution is transferred to a tall cylinder, and the hydrometer, thermometer and containing-vessel are washed with about 5 ml. of water, the difference between this volume and 12·5 ml. being used to dissolve 5·25 g. of potassium iodide and 0·25 g. of iodine. The solutions are mixed well and placed in the dark, and on the next day all the clear liquid except a layer 4 cm. above the sediment, is transferred in a pipette to a black bottle; a scale of iodine is then added.

A correct stain should give the following colours:—rag, cotton, linen or hemp, wine-red or brownish-pink; chemical wood, adansonia, bleached straw and jute, dark blue; mechanical wood, unbleached jute or straw, lemon yellow; esparto, bluish or reddish; manila, varying shades (blue to yellow). The colour differences, however, are only to be regarded as a supplementary aid to the identification of fibres by their characteristic markings.*

(2) *Sutermeister General Stain* (T.A.P.P.I. Methods, *loc. cit.*).—The moistened fibres are stained with a solution containing 1·3 g. of iodine and 1·8 g. of potassium iodide in 100 ml. of water for 1 minute, the excess of stain is removed, and the fibres are treated with a clear, saturated solution of calcium chloride. Cotton, linen, hemp, and ramie appear red or brownish-red; bleached soda pulps from deciduous woods, dark blue; bleached and well-digested unbleached sulphite wood, blue or reddish violet; jute, manila, hemp and lignified unbleached sulphite wood, green; mechanical wood, yellow. An advantage of this stain is that it is not so dark as to obscure the markings on the fibres.

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* Experience has shown that this procedure does not always give the same results; in particular, it is often difficult to distinguish rag and chemical wood fibres by their colours. It has been found desirable to test the stain on fibres of known origin, and to add more zinc chloride if the rag appears too blue or more iodine if the wood appears too red.—J. G.

(3) *Bright's Stain* (Federal Specification, *loc. cit.*).—A mixture of 10 ml. each of 2·7 per cent. ferric chloride ($FeCl_3$, $6H_2O$) solution and 3·29 per cent. potassium ferricyanide solution (filtered) is used to stain the moistened fibres for 20 minutes at 20° ± 1° C. The slide is then dipped into water six times, dried and immersed for 20 minutes in a fresh filtered solution of 3 g. of crude benzopurpurine-4B conc. in 500 ml. of cold water. It is finally washed and dried. Bleached fibres, or fibres practically free from lignocellulose, appear red; unbleached or lignified fibres appear blue.

In the Kantrowitz-Simmons modification (U.S. Govt. Printing Office, *Tech. Bull.*, No. 20, 1934) the procedure is shortened by the use of a 0·5 per cent. solution of the dye in warm 50 per cent. alcohol. This increases the amount of dye dissolved, and the staining-time is only 2 minutes. If the fibres are suspended in the stain, the period of the first staining may be reduced to 1 minute.

(4) *Klemm's Stain.*—The slide is placed in a saturated solution of malachite green in 2 per cent. acetic acid and then washed well. Unbleached (sulphite or sulphate) pulps appear deep green; thoroughly bleached fibres are unaffected; partly-bleached fibres assume intermediate shades (see also Grant, *Proc. Tech. Sect. Paper Makers' Assoc.*, 1935, **16**, 97).

(5) *Alexander's Stain* (*Paper*, 1934, **33**, 138).—The slide is stained for 1 minute with a solution of 0·2 g. of Congo red in 300 ml. of water. It is then dried (without washing) in air, and immersed for 1 minute in 3 drops of a solution of 100 g. of calcium nitrate in 50 ml. of water; 1 drop of Herzberg stain is added, and the mixed stains are allowed to act for three minutes. Coniferous fibres appear pink, and deciduous fibres blue.

With Korn's modification (Federal Specification, *loc. cit.*, and *Papier Fabr.*, 1925, **23**, 781) the fibres are floated in three drops of a solution of 100 g. of calcium nitrate in 25 ml. of water for 1 minute, and 1 drop of Herzberg's stain is then added.

The results are not always reliable for soft cooked, sulphate coniferous pulps. With this exception Korn's method, though simpler, is reliable.

(6) *Lofton–Merritt Stain* (Federal Specification, *loc. cit.*).—The fibres are stained for 2 minutes in a mixture containing 1 volume of a 2 per cent. solution of malachite green and 2 volumes of a 1 per cent. solution of basic fuchsin in water. The excess is blotted off, a few drops of 0·1 per cent. hydrochloric acid are added, and this too is blotted off and replaced by water. Unbleached sulphate fibres are stained blue or blue-green, and unbleached sulphite fibres purple. If tests on samples of known origin produce purple sulphate fibres or green sulphite fibres, more malachite green or fuchsin must be added, respectively (see also, Grant, *loc. cit.*).

(7) *Mitsumata and Gampi.*—These may be distinguished by means of 17·5 per cent. sodium hydroxide solution, as the former shows a bead-like structure due to swelling.

TEXTILE FIBRES

PREPARATION OF THE SAMPLE.—The individual fibres in a sample of a textile may, as a rule, be distinguished easily under the microscope and separated, but if the fibres are dyed to a deep shade this is more difficult, and, moreover, the subsequent staining is affected. The fibres must therefore be decolorised, *e.g.* by means of boiling water or by cold or warm 1 per cent. acid or alkali; sodium hyposulphite ($Na_2S_2O_4$, known in the trade as "hydrosulphite") is very effective. Wool fibres, which hold the dye so tenaciously that they are attacked themselves before they are decolorised, may be treated with a warm mixture of 1 volume of 20 per cent. titanous chloride solution and 2 volumes of conc. hydrochloric acid.

Ignition in a small flame is frequently an aid to identification (*e.g.* casein, animal fibres and acetate rayon give distinctive odours and leave characteristic residues).

(1) ANIMAL FIBRES.—Millon's reagent stains animal fibres a pink colour in 2 minutes; vegetable fibres do not react. A 1 per cent. solution of picric acid produces a yellow colour with animal fibres, but will not stain vegetable fibres. This is a useful confirmatory test, especially for dyed fibres which are incompletely decolorised.

(2) CASEIN FIBRES are stained red by a saturated solution of benzo-purpurine in water (Bergen, *Amer. Dyestuff Rep.*, 1936, **25**, 146), and bright blue by a saturated solution of indigo carmine in very dilute sulphuric acid (Herzog, *Melliand Textilber.*, 1931, **12**, 768).

(3) CORDAGE FIBRES.—(*a*) *Swett's Test* (ANALYST, 1918, **43**, 227) distinguishes manila from all other "hard" rope fibres. The test requires considerable care, and experiments should be made on samples of known origin. It is also important that the alcohol and ammonia are not weakened by exposure to the air, and that prolonged exposure to ammonia fumes (which discharges the red colour) is avoided.

(*b*) *Stegmata Stains.*—The whole ash left on ignition is mounted in aniline oil or phenol; the stegmata or silicified cells of abacia (manila) are then visible as rows of rectangular hollow bodies. The ash of coconut fibres contains siliceous globules which are of various sizes, and have a foam-like inner structure; sisal, however, produces no siliceous skeletons, although characteristic elongated calcareous aggregates are visible. The action of 20 per cent. hydrochloric acid is to render the siliceous structures more readily visible; the formation of needles on addition of sulphuric acid indicates the presence of calcium.

Alternatively, the ash may be dropped into a 2 per cent. solution of potassium ferrocyanide and hydrochloric acid then added. The round stegmata of coconut usually turn blue, whilst a lighter blue is often shown by those of manila.

(*c*) *Jute Stain.*—The fibres are placed in 1 drop of a solution of 1 g. of phloroglucinol in 80 ml. of alcohol, and 1 drop of conc. hydrochloric acid is added. Unbleached jute fibres, which are highly lignified, turn dark violet-red.

(4) COTTON.—(*a*) *Cuprammonium Test* (Muller, *Faserforsch.*, 1929, **7**, 205).—The reagent is a solution of 2 g. of cupric hydroxide in 100 ml. of 25 per cent. ammonia, to which is added a few drops of ruthenium red; it should be kept in a dark bottle. When immersed in a few drops of the reagent cotton swells, forming light blue "balloons" which are separated by constrictions, the remnants of cuticle being pink; mercerised cotton, however, swells uniformly. The method can only be used qualitatively.

(*b*) *Hübner's Stain* (*J. Soc. Chem. Ind.*, 1908, **27**, 105; Lange, *Z. angew. Chem.*, 1903, **16**, 599.)—Mercerised cotton is stained deep blue or black by a 20 per cent. solution of iodine in a saturated solution of potassium iodide; unmercerised cotton is not stained. The method is good, provided that decolorisation has been thorough.

(*c*) *Fluorescence Analysis* sometimes serves to distinguish old and new cotton, since the latter has a violet fluorescence which turns to an ivory or brown colour as it ages. It is advisable to have authentic samples available for comparison. With mixtures the results should be assessed in conjunction with other evidence.

(5) FLAX, HEMP AND RAMIE.—(*a*) *Cross Sections* of the fibres are stained with a 1:10,000 solution of ruthenium red and washed. The cell-contents of flax and the middle lamellae of hemp are stained most prominently, and the respective lumens are circular and elongated.

(*b*) *Cuprammonium* (see above).—As flax swells, remnants of protoplasm are visible in the tortuous central tube, whilst the inner canal of hemp shows horizontal striations. The test is useless for highly-bleached fibres. Swelling may be arrested by transferring the fibre to a mixture of equal volumes of water, glycerin and alcohol.

(*c*) *Cyanin* (Herzog, *Melliand Textilber.*, 1932, **13**, 121, 181).—The fibres are macerated in a boiling 1 per cent. solution of sodium hydroxide and thoroughly washed. They are then stained with a warm mixture of an almost saturated solution of cyanin, to which has been added 33 per cent. of glycerin, and are finally washed in a mixture of equal volumes of glycerin, water and alcohol and mounted in glycerin. Flax fibres remain colourless, but hemp is stained greenish-blue owing to lignification of the middle lamella.

(*d*) *Moisture Test* (Nodder, ANALYST, 1923, **48**, 88).—If a fibre is wetted and drawn between moist finger-tips, and then held vertically and viewed from above, flax moves in a clockwise direction; hemp sometimes does the same, but more usually it moves in the opposite direction, although less vigorously.

(*e*) *Potassium Dichromate* (Hanausek, *Z. Farben-Ind.*, 1908, **7**, 105).—Flax swells more readily than hemp in a solution of potassium dichromate in dilute sulphuric acid; the central canals are wavy and straight, respectively.

(*f*) *Ramie* (Molisch, *Akad. Wiss. Wien., Sitzungsber.*, 1920, (i), **129**, 261).—The fibres are ignited over a low flame, and the whole ash is mounted in aniline. Numerous characteristic spherical cystoliths with spicules are prominent. The cystoliths of manila are smaller, and characteristic rows of stegmata are apparent (see above); flax has neither cystoliths nor stegmata.

(6) RAYONS.—The results of Tests (*a*) to (*k*) are summarised in the Table. Italics indicate the respect in which any one particular rayon differs from all the others, and the corresponding test is therefore specially suitable for identification of such rayons. Special treatments (*e.g.* delustring and "ironproofing") and experimental rayons not commonly found on the market at present, may provide deviations from these results. Tests (*d*), (*e*) and (*f*) are the most satisfactory for quantitative work.

(*a*) *Acetone* (A.S.T.M., *Standards on Textile Fibres*, 1937, p. 36) is added to the fibres, which are observed under the microscope.

(*b*) *Diphenylamine* (0·3 g.) is dissolved in 20 ml. of conc. sulphuric acid and 10 ml. of glacial acetic acid (*ibid.*, pp. 33 and 36), and the reagent is added to the fibres on a slide.

(*c*) *Erie Fast Orange-CG* (a 0·2 per cent. solution) is allowed to stain the fibres for 3 minutes, and the fibres are then washed and examined. A rise in temperature during staining deepens the colour (*ibid.*, p. 36; Hahn, *Text. Col.*, 1931, **53**, 487).

(*d*) *Wright's Stain* (Johnson, *Text. World*, 1929, **75**, 49).—A suspension of methylene blue-2B in water is precipitated with about one-half the quantity of "eosin yellowish" (? Colour Index No. 768), and the mixture is stirred well. The precipitate is separated in a centrifuge and, subsequently, by decantation or filtration. A white or light-coloured sample of the dry fibre is covered with a cold solution of the stain* in alcohol, which is boiled for a few seconds. The fibres are then washed and examined. All rayons give a violet colour if wet before being stained.

(*e*) *Hahn's Picric Acid Test* (*Text. Col.*, 1931, **53**, 487).—The sample is immersed for 3 minutes in a cold or luke-warm solution containing 1 per cent. of picric acid and 0·2 per cent. of Soluble Blue-2B extra; it is then washed well.

(*f*) *Hahn's Eosin Test* (*loc. cit.*).—To a cold solution of 0·2 g. of Soluble Blue-2B extra, 0·1 g. of eosin and 1 g. of tannic acid in 100 ml. of hot water is added 0·2 ml. of 10 per cent. hydrochloric acid. The staining-period is 3 minutes, after which the fibres are washed.

(*g*) *Iodine* (0·015 g.) is dissolved in 1 litre of a 5 per cent. solution of potassium iodide and 2 drops of acetic acid are added (Kasche, *Melliand Textilber.*, 1932, **13**, 420). The fibres are immersed and then washed.

(*h*) *Dark-Field Illumination* (magnification, 350 diameters).—Large, brilliantly-reflecting particles, derived from delustrants, may occur in all rayons; however, they are not usually confused with the particles referred to in the Table.

(*i*) *Silver Nitrate* (Levey, *Chemist-Analyst*, 1936, **25**, 14).—To a solution containing 4 g. of sodium thiosulphate is added a solution containing 1 g. of silver nitrate until the cloudiness disappears; a solution containing 4 g. of sodium hydroxide is then added, the mixture is diluted to 100 ml., and the final solution is cooled and filtered. Staining is carried out at the boiling-point.

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* *i.e.* presumably the above-mentioned precipitate.—J. G.

(*j*) *Polarised Light.* See Table.

(*k*) *Cross-Sections* (A.S.T.M., *loc. cit.*; Rayon Committee, *Proc. Amer. Assoc. Text. Chem. Colorists*, **1934**, **23**, 241).—See Table; photomicrographs are given in the references.

	TYPE OF RAYON			
Test	Cellulose acetate	Viscose	Cuprammonium	Nitrocellulose
(*a*)	*Dissolves*	Unaltered	Unaltered	Unaltered
(*b*)	Colourless; dissolves	Colourless; dissolves	Colourless; dissolves	*Deep blue*; dissolves
(*c*)	Colourless or pale orange	Colourless or pale orange	*Deep orange*	Colourless or pale orange
(*d*)	Violet (partly disintegrated)	*Blue*	*Violet*	Deep blue
(*e*)	Yellow	Colourless	*Blue*	Colourless
(*f*)	Lavender	Lavender	*Blue*	Lavender
(*g*)	*Yellow*	Almost colourless	Almost colourless	Almost colourless
(*h*)	Almost transparent	*Innumerable very fine white particles*	Almost transparent	Almost transparent
(*i*)	Colourless	*Brown*	Colourless	Brown
(*j*)	*Silver gray*	Streaked	*Uniform* yellow or green	Streaked
(*k*)	Few indentations	*Serrated edges*	*Circular*	Few indentations

(7) SILK.—The precipitate formed by the addition of sodium hydroxide solution to a solution of 25 g. of crystalline nickel sulphate in 500 ml. of water, is washed and subsequently dissolved in a mixture of 125 ml. each of conc. ammonia and water. Ordinary silk fibres swell and dissolve in the cold, whilst "wild" (tussah) silk is unaffected, although it behaves similarly to ordinary silk on warming.

(8) WOOL (Herzog, *Melliand Textilber.*, **1931**, **12**, 768).—The fibres are stained in a saturated solution of indigo carmine in very dilute sulphuric acid, which is prepared in the cold; they are then mounted in conc. glycerin. Only the damaged portions of wool become bright blue. If the specimen is counter-stained with picric acid before being mounted, the undamaged parts become yellow and the damaged parts green. Damage caused by mechanical means, treatment with alkali or exposure to light is detectable in this way. J. G.

The International Standard for the Gonadotrophic Substance of Human Urine of Pregnancy: Chorionic Gonadotrophin

WE have been asked by the Director of the Department of Biological Standards, National Institute for Medical Research, to publish the following statement:

> At the Third International Conference on the Standardisation of Hormones, held at Geneva on August 11th to 13th, 1938, it was decided that international standards should be established for certain hormones of the anterior lobe of the pituitary gland and analogous substances found in urine and serum, and that international units should be defined in terms of a weight of each such standard.
>
> It was further decided that the final preparation of these standards, their dispensing in a form suitable and convenient for the use of the laboratory worker, and their storage, preservation and subsequent distribution should be undertaken by the National Institute for Medical Research, Hampstead, London.

We are asked to announce that the preparation of the international standard for the gonadotrophic substance of human urine of pregnancy (chorionic gonadotrophin) has now been completed. The standard has been prepared from substantial amounts of material generously provided by six firms in different countries. The individual samples having been approved by the Conference, a mixture was made and the standard has been finally dispensed in the form of 10 milligram tablets and packed in a very convenient manner.

The international unit has been defined as the specific gonadotrophic activity of 0·1 milligram of the standard preparation, an amount of activity similar to that required, under the conditions used by many workers, to cause cornification of the vaginal epithelium of the immature rat. Each tablet contains approximately 100 international units.

As in the case of the international standards for other hormones, drugs and vitamins, the international standard for the gonadotrophic substance of human urine of pregnancy (chorionic gonadotrophin) is held, on behalf of the Health Organisation of the League of Nations, at the National Institute for Medical Research, Hampstead, London, and is distributed therefrom to national control centres established in other countries for local distribution to laboratories, institutes and research workers; and to workers in other countries in which the establishment of national control centres has not yet been completed.

With regard to the supply of the standard for chorionic gonadotrophin to those requiring it in the United Kingdom, application should be made to the Department of Biological Standards, National Institute for Medical Research, Hampstead, London, N.W.3.

British Standards Institution

THE following Standard Specifications have been issued*:

NO. 135—1939. BRITISH STANDARD SPECIFICATIONS FOR BENZOLES. (PURE BENZOLE, PURE BENZOLE FOR NITRATION, MOTOR BENZOLE, 90'S BENZOLE, INDUSTRIAL BENZOLE.)

These Specifications are based on the Standard Specifications Nos. 1, 2, 3, 4 and 5, 1938, respectively, of the National Benzole Association.

NO. 458—1939. BRITISH STANDARD SPECIFICATIONS FOR XYLOLES. (2° XYLOLE, 3° XYLOLE, AND 5° XYLOLE.)

These Specifications are based on the Standard Specifications Nos. 9, 10 and 11, 1938, respectively, of the National Benzole Association.

NO. 805—1939. BRITISH STANDARD SPECIFICATIONS FOR TOLUOLES. (PURE TOLUOLE, PURE TOLUOLE FOR NITRATION, 90'S TOLUOLE, 95'S TOLUOLE.)

These Specifications are based on the Standard Specifications Nos. 6, 7, 8A and 8B, 1938, respectively, of the National Benzole Association.

NO. 479—1939. BRITISH STANDARD SPECIFICATIONS FOR COAL TAR NAPHTHAS (COAL TAR SOLVENT NAPHTHAS 96/100 AND 90/160, COAL TAR HEAVY NAPHTHA 90/190, COAL TAR HEAVY NAPHTHAS [UNRECTIFIED] 90/190 AND 90/200.)

The methods of testing and descriptions of apparatus given for the preceding four Specifications are those recommended by the Standardisation of Tar Products Tests Committee and issued in their publication "STANDARD METHODS OF TESTING TAR AND ITS PRODUCTS."

NO. 830—1939. BRITISH STANDARD SPECIFICATION FOR WINCHESTER BOTTLES (OF 80 OZ. AND 90 OZ. NOMINAL CAPACITY).

The Specification refers to the most usual sizes of Winchester bottles, one of 80 fluid ounces nominal capacity to meet the requirements of those who need a bottle to contain safely half a gallon of liquid and a larger bottle suitable for liquids sold by weight, which will allow a reasonable expansion and vapour space. The nature of the liquid will determine the volume of that liquid for which the bottle is suitable. The Specification provides for these sizes of bottle, either plain or fluted, with four alternative methods of closure. Screw stoppers and caps and corks should be used with due regard to the nature of the liquid to be contained in the bottles fitted with them. To facilitate storage and packing, the same diameter has been adopted for the two sizes of bottle, the two capacities being secured by a variation in the height.

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* Obtainable from the Publication Department British Standards Institution, 28 Victoria Street, London, S.W.1. Nos. 135, 458, 479, and 805, price 3s. 6d. net, post free 3s. 8d. Nos. 830, and 836, price 2s. net, post free 2s. 2d.

To allow of small variations in shape resulting from differing methods of manufacture, the shapes of the bottles are not standardised in detail, and for similar reasons no requirements are laid down as to the minimum thickness of the glass. A minimum weight of glass, however, is specified (40 and 44 oz. for 80 and 90 fluid oz. bottles, respectively), and it should be the aim of manufacturers to secure a reasonably uniform distribution of the glass and to avoid abrupt variations in thickness.

No. 836—1939. British Standard Specification for Whale Oil.

This Specification forms part of a series of British Standards for Marine Animal and Fish Oils, the preparation of which was authorised by the Chemical Divisional Council.

The Specification is intended to include the technical provisions necessary for the supply of the material to which it refers, but does not purport to include all the necessary provisions of a contract.

It does not provide for all grades of good whale oil of merchantable quality, some oils being of higher and some of lower grade than that provided for in the Specification.

Whale oil is defined as the product obtained from various parts of the whale (excluding sperm oil). It must be free from contamination or admixture with other oils and fats, and shall answer to the following requirements:

Moisture and dirt.—Not more than 0·5 per cent. of moisture and/or dirt shall be present when determined by the methods described. An apparatus for the determination is described and illustrated.

Colour.—When the liquid-filtered oil is matched in a 1-in. cell with Lovibond glasses at 25° to 30° C., the red component of the glasses shall not exceed 6 units. In preparing oil for this test it is essential that the temperature shall not materially exceed 30° C.

Saponification value.—Not lower than 182 or higher than 205 when determined by the specified method.

Acidity.—The oil shall be free from mineral and added organic acids. Its acidity, when determined by the specified method, shall not exceed 6 per cent. of free fatty acids calculated as oleic acid.

Unsaponifiable matter.—The oil shall not contain more than 2·0 per cent. as determined by the Society of Public Analysts' method (ANALYST, 1933, 58, 203).

Sampling and size of sample.—Representative samples, each measuring not less than 400 ml., shall be taken, wherever possible in triplicate, from original containers or from the bulk, and shall be packed in clean, dry air-tight, non-absorbent containers, on which the sample has no action. The containers shall be of such a size that they are nearly filled by the sample.

Recommended methods for sampling fats and fatty oils are given in B.S. No. 627—1935.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Phosphorus in Fruits and Fruit Products. H. W. Gerritz. (*J. Assoc. Off. Agric. Chem.*, 1939, **22**, 131–137.)—Zinzadze's method has been adapted to the use of the neutral wedge photometer (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 130) and to the analysis of samples prepared by wet ashing. (1) *Zinzadze's reagent.*—The directions and precautions given by Zinzadze (*cf.* ANALYST, 1932, **57**, 411; 1936, **61**, 198) are followed exactly, a ten-fold dilution being used in the actual determination. (2) *Preparation of sample.*—A portion of the sample containing 1 to 3 mg. of phosphorus pentoxide is transferred to a 500-ml. Kjeldahl flask. For the determination of phosphorus in the water-soluble portion of fruits and fruit juices 25 ml. (equivalent to 3·75 g.) of the sample solution prepared according to the official methods (*Methods of Analysis, A.O.A.C.*, 1935, XXVI, [*b*] or [*c*] are used, and for jams and jellies 50 ml. of the prepared solution. Fifteen ml. of conc. nitric acid, 5 ml. of conc. sulphuric acid, 5 or 6 small glass beads, and a few pieces of broken porcelain are added, and the liquid is boiled over a moderate flame until copious fumes of sulphuric acid are evolved. If there is pronounced charring, the liquid is cooled slightly and a little more nitric acid is cautiously added (with jams 3 additions of the acid may be necessary). The liquid is boiled again until fumes are evolved, 0·5 ml. of 60 per cent. (reagent quality) perchloric acid is added, and the "fuming" is continued for a few minutes. The digest should now be colourless or slightly greenish-yellow. If necessary, a further 0·5 ml. of the perchloric acid is added and the "fuming" is continued for 3 or 4 minutes. The liquid is cooled somewhat, 50 ml. of water are added, and the solution is boiled until fumes appear, to remove traces of nitric acid, after which it is cooled, treated with 25 ml. of water, made up to 100 ml. and thoroughly mixed. (3) *Determination of phosphorus*.—Twenty ml. are transferred to a 100-ml. flask (a Kohlrausch sugar flask has been found convenient) with a mark at 60 ml. Three drops of sodium alizarin sulphonate solution (0·20 g. of sodium alizarin monosulphonate dissolved in 100 ml. of water and filtered) are added, and the liquid is neutralised with conc. potassium hydroxide solution (prepared from phosphate- and arsenate-free potassium hydroxide and stored in a paraffin-lined container); the colour of the liquid is adjusted to yellow by means of *N* potassium hydroxide solution and *N* sulphuric acid, each being added dropwise with constant mixing until a single drop of the sulphuric acid just changes the colour to yellow. The liquid is diluted to the 60-ml. mark and mixed. The flask is placed in a boiling water-bath and brought to that temperature, a drop or two of the *N* sulphuric acid being added if the colour becomes pink. Exactly 10 ml. of Zinzadze's reagent (10-fold dilution) are added, the liquid is mixed, and the heating in the bath is continued for exactly 20 minutes. (It is important that the standards and unknown solutions be heated at the same temperature.) The solution is cooled, diluted and mixed, and the colour intensity is measured by means of the neutral wedge photometer, with a 1-inch cell and No. 66 filter (4·5 MM Corning dark pyrometer red No. 241; with B & L "Smoke C" glass, wedge filter 65, *i.e.* the same as 66 plus a half MM of Jena BG18, is used) and Jena 0–2 neutral wedge. The method covers a range up to 0·6 mg. of phosphorus pentoxide in the final 100 ml. of solution. Standards covering this range are prepared by placing 0, 2, 4, 6, 8, 10 and 12 ml. of standard phosphate solution containing 0·05 mg. per ml. (prepared by dissolving 0·1917 g. of pure dry potassium dihydrogen phosphate in about 200 ml. of water, adding 10 ml. of *N* sulphuric acid and 6 drops of 0·1 *N* potassium permanganate solution, and diluting to 2 litres) in 100-ml. flasks with marks at 60 ml. Two ml. of dilute (1 : 1) sulphuric acid and 3 drops of the indicator are introduced into each flask, with water to make about 20 ml. These standards are then treated in the same way as the sample, beginning with the neutralisation, developing the colour, cooling, making up to volume, and determining the colour intensity in the neutral wedge photometer. If alkali of suitable purity has been used, the 0 standard should give a reading not more than 10 to 15 mm. greater than the reading with pure water. A large-scale graph of the standards is made, mg. of phosphorus pentoxide being plotted against photometer readings. The sample photometer readings are converted into mg. of phosphorus present in the final 100-ml. portion by means of this graph. The photometer need be calibrated only once for each batch of reagents if the adjustment is not altered. In the analysis of heterogeneous samples, *e.g.* fresh fruit, for total phosphorus, it may be necessary to digest a larger portion in order to eliminate sampling and weighing errors. It is then convenient to take double the sample (7·5 g.) and add double the volume of sulphuric acid (10 ml.). The digest is made up to 200 ml. and a 20-ml. aliquot part is transferred to a 100-ml. flask for colour development. The weight of sample digested may be varied to suit the nature of the sample, provided that the final 20-ml. portion contains about 1 ml. of sulphuric acid and 0·2 to 0·6 mg. of phosphorus pentoxide. The method has been found to be applicable to the analysis of materials of higher phosphorus-content, such as semolina macaroni. Zinzadze mentions that iron, nitrate and arsenic interfere with the development of the colour with his reagent. Nitrates are not present in solutions prepared as described, and neither iron nor arsenic is ordinarily present in sufficient quantity in fruit or fruit products to cause interference. If fruit were contaminated with spray residue to the extent of, say, 0·1 grain of arsenic trioxide per lb., it would make a positive error in the phosphate determined of only 1·4 mg. per 100 g. If the presence of excessive quantities of iron or arsenic is suspected the procedure is modified as follows:—The above directions are followed to the point "until a single drop of the sulphuric acid just changes the colour to yellow." Ten ml. of exactly *N* sulphuric acid and 10 ml. of 8 per cent. sodium bisulphite solution are added, and the solution is diluted to 60 ml. The flask is heated in a boiling water-bath for 1 hour and the directions given above are then followed, beginning "Exactly 10 ml. of Zinzadze's reagent (10-fold dilution) are added." The standards must, of course, then be treated in the same manner (see also Abstract, p. 455). E. M. P.

Contamination of Parsley with Arsenic. J. M. Rowson and C. E. Waterhouse. (*Pharm. J.*, 1939, **142**, 329.)—The arsenic-content of a sample of dried parsley (leaf and a little stalk) was 6 p.p.m. That of the herb before drying was: leaf and stalk, 1; root (with a little adhering earth), 1·5 p.p.m. (washing the fresh herb very thoroughly before analysis did not alter this result), and for a similar sample from a different locality it was 3 p.p.m. As fresh parsley normally loses from 60 to 80 per cent. of its weight on drying, the arsenic must have been present in the original sample. Cultivation experiments are in progress to investigate the possibility of the assimilation of arsenic by parsley. E. B. D.

Unusual Adulterant of Olive Oil (Quinoline Yellow). J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1939, **77**, 254–256.)—A specimen of olive oil described as "guaranteed pure and genuine extra vierge" gave constants differing little from the normal values for genuine olive oil, but when examined in ultra-violet light the sample showed an intense grass-green fluorescence. Parallel determinations were therefore made with two samples of olive oil of French origin and a sample of tea-seed oil of Chinese origin. The "guaranteed pure" oil showed great similarity to pure olive oil and to tea-seed oil and, since it did not answer to tests for arachis, sesame, cotton-seed or kapok oil, suspicion was aroused that it was a mixture of olive and tea-seed oils. The possibility of its consisting entirely of tea-seed oil was excluded by the m.p. of the phytosteryl acetate prepared from it, *viz.* 120° C., the m.p. of phytosteryl acetate prepared from tea-seed oil being 156 to 157° C. In the fractional precipitation of its fatty acids (Kreis and Roth, *Z. Unters. Nahr. Genussm.*, 1913, **25**, 84) the sample yielded only 0·68 g. of solid fatty acids from 20 g. of oil, whereas pure olive oil should yield at least 2·2 g. Another suspicious feature was the fact that the lead salts began to separate in 4 hours, as with tea-seed oil, whereas with pure olive oil the separation begins within an hour. These results pointed to the presence of a considerable amount of another oil, possibly tea-seed oil. In addition, the oil contained an artificial dye which was not detected by the usual methods (*Schweiz. Lebensmittelbuch*, 4th Ed., Bern, Zimmermann & Co., 1937), but was detectable by the method of Lecoq and Prince (*Guide pratique d'Analyses alimentaires*, Paris: Vicot Frères, 1921). The oil (5 g.) was dissolved in 5 ml. of petroleum spirit, the solution was shaken with 5 ml. of glacial acetic acid, and the acid layer was separated and evaporated to dryness. A deep yellow residue was obtained. It was not possible to identify the dye by dyeing tests, but when the fluorescence of the oil in ultra-violet light was compared with that of a series of dyes dissolved in almost colourless arachis oil, the conclusion was reached that the dye was quinoline-yellow. A. O. J.

Water Melon Seed Oil. A. J. Nolte and H. W. von Loesecke. (*J. Amer. Chem. Soc.*, 1939, **61**, 889–891.)—Air-dried seeds of melons (culls) grown in south central Florida, of the variety Cuban Queen (*Citrullus vulgaris*), a round or slightly oval melon with brownish black seeds, had the following composition:—moisture, 8·84; fat (ether extract), 26·52; protein, 17·31; ash, 2·36 (water-soluble, 0·05; insoluble, 2·31); undetermined, 44·97 per cent. The yellowish-brown oil was extracted with petroleum spirit and filtered; it contained 0·06 per cent. of volatile constituents and had the following characteristics:—sp.gr. at 25/25° C., 0·9197; n_D^{20}, 1·4669; saponification value, 197·4; iodine value (Hanus), 133·8; Reichert-Meissl value, 0·29; Polenske value, 0·72; acetyl value, 7·5; Hehner value, 89·2; acid value, 0·42; unsaponifiable matter, 1·19 per cent.; unsaturated acids (corr.), 78·96 per cent., with iodine value, 166·6; saturated acids (corr.), 14·56 per cent. The fatty acids consisted of palmitic, 8·84; stearic, 5·61; arachidic, 0·72; oleic, 13·03; linolic, 68·38 per cent. D. G. H.

Seed Fat of *Hodgsonia capniocarpa*. T. P. Hilditch, M. L. Meara and W. H. Pedelty. (*J. Soc. Chem. Ind.*, 1939, **58**, 26–29.)—The seed kernels of this plant, which is a Malayan climber of the Natural Order *Cucurbitaceae*, yielded to petroleum spirit 62 per cent. of a pale yellow oil with saponification equivalent 284·3, iodine value 65·5, acid value 0·8, and unsaponifiable matter 0·3 per cent. The component acids were found to consist of myristic, 0·7; palmitic, 39·5; stearic, 8·3; arachidic, 0·7; hexadecenoic, 1·0; oleic, 26·0; linolic, 23·8 per cent. mol. The chief constituents of the fat were found to be: "oleo"dipalmitins, 33; "oleo"-palmitostearins, 27; palmito-di"oleins," 24; tri-unsaturated glycerides (oleo-linolins), 13 per cent. mol., with possibly very small quantities of stearo-di"oleins." A small proportion (2·5 per cent.) of fully-saturated components was present. The occurrence of 13 per cent. of tri-unsaturated glycerides is distinctive, owing to the fact that oleic and linolic acids are both present in about the same high proportion. A comparison of the fatty acids with the component acids of shea butter, in which the ratio of unsaturated to saturated acids is very similar, but in which linolic acid forms only a very minor proportion of the unsaturated group, gave:—fully saturated (*a*) shea butter, 4·5; (*b*) *H. capniocarpa*, 2·5; mono-unsaturated, (*a*) 34·5, (*b*) 60; di-unsaturated mono-saturated, (*a*) 56·5; (*b*), 24; and tri-unsaturated, (*a*) 4·5; (*b*), 13 per cent. The specific nature of the glycerides in this fat is evidently the result of combinations of four major component acids (palmitic, stearic, oleic, and linolic) to form triglycerides, whereas in fats previously studied it has been necessary to consider only the three acids, palmitic, stearic and oleic. D. G. H.

Chemical Examination of *Bragantia wallichii* (Lour). B. L. Manjunath and M. S. Shankara Rao. (*J. India Chem. Soc.*, 1938, **15**, 646–648.)—The root of *Bragantia wallichii*, Lour. (Sanskrit Chakrani, N. O. *Aristolochiaceae*, growing in the Western Ghats) has been used in the proportion of 4 g. of root made into a paste with 14 ml. of lemon juice, with beneficial results, in cases of cholera and diarrhoea. Fifty g. of powdered root were successively extracted with solvents and yielded extracts as follows: petroleum spirit, 0·48; ether, 0·78; chloroform, 0·49; ethyl acetate, 0·48; absolute alcohol, 3·70 per cent. Constituents volatile in steam amounted to 0·05 per cent., and 0·03 per cent. of alkaloid was present. About 50 kg. of root were extracted, and the extracts were examined in detail. The fatty acids of the dark brown oil from the petroleum spirit extract were palmitic, a small amount of crude lignoceric, oleic and linolic. A yellow substance separated from the ethereal extract, and the ethereal solution was successively extracted with 5 per cent. hydrochloric acid, potassium bicarbonate, potassium carbonate and potassium hydroxide solutions. The hydrochloric acid extract was combined with the hydrochloric acid extract of the chloroform extract, and these gave positive tests with reagents for alkaloids. The yellow substance, which was also obtained on acidifying the alkali extracts from ether and chloroform, and from the ethyl acetate extract, was identified as *iso*aristolochic acid after crystallisation from glacial acetic acid and alcohol. Unlike the acid itself, the methyl derivative was tasteless. D. G. H.

Action of Strychnine and Quinine on Bordeaux B. D. B. Dott. (*Pharm. J.*, 1939, **142**, 328–329.)—As previously stated (*Pharm. J.*, 1938, **141**, 261; Abst., ANALYST, 1938, **63**, 827) the strychnine separated from compound syrup of glycerophosphates is yellow even after re-precipitation with ferrocyanide, owing to the formation of a compound of strychnine with the acid of Bordeaux B. Also, the strychnine cannot be correctly determined by titration. It may be crystallised from the impure precipitate by extraction of a benzene solution with water and acid followed by addition of alkali and extraction with chloroform and evaporation, this process being repeated if necessary. When solutions containing equivalent quantities of strychnine hydrochloride and the dyestuff (termed sodium azorubrate) are mixed, part of the strychnine is precipitated as an azorubrate and part remains in the filtrate, which is coloured red. Analysis by two methods (*a*) and (*b*), showed that the precipitate contained (*a*) 52·06 and (*b*) 52·31 per cent. of strychnine. Theoretically, the di- and mono-strychnine salts contain 59·43 and 42·22 per cent. respectively of alkaloid. With quinine hydrochloride solution the dye gave a precipitate containing 57·0 per cent. of quinine (theoretical for di-quinine salt, 58·69 per cent.). It is considered therefore that Bordeaux B should not be used for colouring liquids containing strychnine or other precipitatable alkaloids. Solubilities in water at room temperature:—strychnine azorubrate, 1 : 1000; quinine azorubrate 1 : 2270. E. B. D.

Valerian: A New Alkaloid. J. J. Blackie and D. Ritchie. (*Pharm. J.*, 1939, **142**, 299–300.)—A water-soluble base possessing physiological activity is present in appreciable quantity in dried valerian root. The base is soluble in cold or hot water and in alcohol, very sparingly soluble in ethyl acetate, and insoluble in acetone, chloroform or ether. It is precipitated by ether in flocculent particles from its solution in amyl alcohol. It has not yet been found possible to crystallise the base or to prepare crystalline derivatives. When distilled in a high vacuum (0·01 mm.) it decomposes at 200° C. Apparently it is not a pyrrole derivative, the presence of which in the root was reported by Cionga (*Comptes rend.*, 1935, **200**, 780), as the vapours evolved on heating the base with zinc dust did not give the characteristic red colour on pine wood. Intravenous injection of the base into a cat under urethane anaesthesia caused a fall in blood pressure, with a secondary effect upon the heart; it also had an inhibitory effect on peristalsis. These physiological effects require confirmation when the base has been obtained in a pure condition. Methods of separating the base from the root by extraction with amyl alcohol after removal of oil, resins, etc., are described in detail. E. M. P.

Methyl Alcohol Content of Tobacco Leaf and Ribs. W. Preiss. (*Z. Unters. Lebensm.*, 1939, **77**, 272–281.)—It has been shown by numerous workers that tobacco smoke contains methyl alcohol derived mainly from methyl pectic esters, and it is generally agreed that the methyl alcohol yield from unfermented tobaccos may reach 0·9 per cent., and that during fermentation that of cigar tobacco is reduced to 0·04—0·2 per cent. and that of cigarette tobacco to about 0·5 per cent., so that, as a rule, the pale tobaccos yield more methyl alcohol than the dark tobaccos. When the coarser parts of the leaf (midrib and large veins) are used, Neumann-Wender (*Münch. Med. Woch.*, 1933, **80**, 737) observed an increased yield of methyl alcohol, constituting a potential source of danger to the smoker. Since the pectic esters are largely responsible for the methyl alcohol occurring in the smoke, it appears necessary to determine the amounts of pectin and lignin and the methyl alcohol derived from them. Also, a determination of methyl alcohol derived from lignin would indicate the proportion of woody tissue in the tobacco. Methods based upon those of von Fellenberg (*Biochem. Z.*, 1918, **85**, 45, 118) were used to distinguish between the methyl alcohol derived from these two sources. To determine the methyl alcohol derived from pectin, 1 g. of finely powdered tobacco was treated with 20 ml. of water and allowed to stand for 2 hours. The mixture was treated with 5 ml. of 10 per cent. sodium hydroxide solution, allowed to stand overnight, and after the addition of 2·5 ml. of 20 per cent. sulphuric acid, it was distilled until 18 to 19 ml. had been collected. This distillate, after the addition of 1 ml. of 20 per cent. sulphuric acid, was redistilled until 14 to 15 ml. of distillate had been collected. To this distillate 5 drops of 10 per cent. sodium hydroxide solution and 5 drops of 10 per cent. silver nitrate solution were added, and 12 ml. of distillate were collected. Finally, this distillate was redistilled from animal charcoal until exactly 10 ml. had been collected. An aliquot portion (3 ml.) was taken for the determination of methyl alcohol. For the determination of the total methyl alcohol from pectin and lignin, 0·5 g. of powdered tobacco was mixed with 15 ml. of 72 per cent. sulphuric acid and boiled gently in a distillation apparatus at such a rate that not more than 1 or 2 ml. of distillate were collected in 10 minutes. When the liquid had cooled, 25 ml. of water were added, and 27 to 28 ml. were distilled. The distillate was neutralised to litmus paper with 10 per cent. sodium hydroxide solution and, after the addition of 5 drops in excess and 5 drops of 10 per cent. silver nitrate solution, the mixture was distilled, and 20 to 21 ml. of distillate were collected. The treatment with sodium hydroxide and silver nitrate was repeated, and the distillate of 12 ml. was redistilled from animal charcoal until exactly 10 ml. of distillate were obtained; an aliquot portion (3 ml.) of this was used for the determination of methyl alcohol. The methyl alcohol concentrates (3 ml.) obtained by these methods were treated in 100-ml. flasks with 1 ml. of alcoholic sulphuric acid (20 ml. of absolute alcohol and 40 ml. of conc. sulphuric acid diluted with water to 200 ml.) and 1 ml. of 5 per cent. potassium permanganate solution, shaken well, allowed to stand for exactly 2 minutes, and treated with 1 ml. of 8 per cent. oxalic acid solution and 1 ml. of conc. sulphuric acid. As soon as the solution became colourless, 5 ml. of fuchsin-sulphurous acid solution (5 g. of fuchsin, 12 g. of crys. sodium sulphite and 100 ml. of *N* sulphuric acid diluted to 1 litre) were added. The solution was allowed to stand for exactly one hour, water was added (25 ml. for amounts up to 1 mg. of methyl alcohol in 10 ml. of distillate, 50 ml. for larger amounts), and the solution was compared in a colorimeter with standard solutions prepared from pure methyl alcohol treated in the same manner. The amount of methyl alcohol present was determined by means of a calibration curve constructed for the instrument. The Lange photo-electric colorimeter is recommended. The methyl alcohol derived from pectin bodies is very small in the large-leaved tobaccos of the alkaline group; in European pipe-tobacco it may reach about 0·4 per cent. Tobacco ribs yield less pectin methyl alcohol than the whole or stripped leaf. In oriental cigarette tobaccos of the acid group the pectin-methyl alcohol content is higher than in the alkaline group and amounts to about 0·5 per cent. Methyl alcohol derived from lignin amounts to about 0·2 per cent. in the large-leaved tobaccos, 0·4 per cent. and more in the ribs, and 0·12 per cent. in the stripped leaves. Oriental tobaccos yield about 0·1 per cent. of methyl alcohol from lignin. The amount of lignin methyl alcohol obtained is a measure of the lignified tissue in the tobacco product and may be used to determine approximately the amount of rib and vein present. The methods described provide a useful means of following the effects of the processes of tobacco manufacture upon its pectin and lignin contents.

A. O. J.

Biochemical

Estimation of Sulphanilamide in Biological Fluids. A. E. A. Werner. (*Lancet*, 1939, 1, 18–20.)—When a solution of sulphanilamide is treated with *p*-dimethylaminobenzaldehyde a deep yellow colour is produced, or, if sufficient sulphanilamide is present, an orange precipitate. The colour of the yellow solution is remarkably stable, is proportional to the concentration of sulphanilamide, and is sensitive to about 1 part in 500,000. It develops rapidly in solutions diluted 1 in 100 or 1 in 200, at which dilutions the normal constituents of urine do not interfere.

Determination in urine.—The urine is diluted with distilled water, so that the solution contains 0·5 to 1·5 mg. of sulphanilamide per 100 ml. To 9 ml. of this solution is added 1 ml. of a 3 per cent. solution of *p*-dimethylaminobenzaldehyde in 7 per cent. sulphuric acid. The yellow colour develops immediately and is compared directly with the colours developed by standard solutions under the same conditions. Sulphanilamide is partly eliminated from the body as the acetyl derivative, and to determine the amount of the drug present in this form, 1 ml. of the urine is heated with 2 ml. of *N* hydrochloric acid for 30 minutes in a boiling water-bath, cooled, neutralised with 2 ml. of *N* sodium hydroxide solution and diluted to 10 ml. This solution is suitably diluted, and 9 ml. are treated with 1 ml. of the *p*-dimethylaminobenzaldehyde reagent to determine the amount of total sulphanilamide; the difference between the free and total amounts gives the amount present as acetylsulphanilamide.

Estimation in blood.—One ml. of oxalated blood is added drop by drop from a pipette to 4 ml. of a 5 per cent. solution of trichloroacetic acid, and the resulting suspension is filtered. Two ml. of the filtrate are transferred to a graduated cylinder and diluted to 3·5 ml. with 0·25 *N* sodium hydroxide solution, and 0·5 ml. of the *p*-dimethylaminobenzaldehyde reagent is added. The colour is compared with the colours of standard solutions as before. To estimate total sulphanilamide, 2 ml. of the acid filtrate are heated in boiling water for 30 minutes and then neutralised and treated with the reagent. For accurate work a colorimeter can be used, as the intensity of the colour is strictly proportional to the concentration for the range 0·25 to 1·5 mg. per 100 ml. For approximate work a simple comparator can be used. Quantitative recoveries were obtained of sulphanilamide and acetyl sulphanilamide added to urine, and of sulphanilamide added to blood. There appeared to be some adsorption of acetylsulphanilamide, however, by the proteins precipitated from blood, but the adsorption was reduced to a minimum by adding 0·5 ml. of blood to 4·5 ml. of trichloroacetic acid solution. Two of the most important derivatives of sulphanilamide, namely, M. & B. 693 (2-sulphanilylaminopyridine) and Uleron (4′-dimethylaminosulphamido-4-aminobenzenesulphonamide) can also be estimated with the same degree of accuracy and sensitivity by this method. F. A. R.

Photometric Determination of Selenium in Tissues and Faeces. R. A. Gortner and H. B. Lewis. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 198–200.)—Horn's modification of the codeine sulphate reaction has been applied. The dry fat-extracted sample is digested in a Kjeldahl flask by heating with sulphuric acid (40 ml.) and yellow mercuric oxide (0·2 g.) until clear. The liquid is diluted to 50 ml. with conc. sulphuric acid, centrifuged for 15 to 20 minutes at 1800 r.p.m., and to 10 ml. are added 3 drops of saturated aqueous codeine sulphate solution. The mixture is kept for 7 hours in the dark, and the intensity of blue colour developed is determined photometrically by means of a Zeiss-Pulfrich photometer fitted with a yellow filter (S.57), which has been calibrated with solutions containing known amounts of selenium treated in a similar manner. Amounts of selenium down to 0·1 mg. were accurately determined. S. G. C.

Direct Colorimetric Method for the Estimation of Inulin in Blood and Urine. A. S. Alving, J. Rubin and B. F. Miller. (*J. Biol. Chem.*, 1939, **127**, 609–616.)—Inulin gives an intense, clear blue colour with alcoholic diphenylamine in hot acid solution, and this reaction has been made the basis of a method of estimating inulin. Since, however, fructose, and to a small extent glucose, give similar colours with the reagent, for accurate determinations these sugars must be removed by fermentation. A suspension of washed yeast cells (0·5 or 1 ml., respectively) is added to 5 or 10 ml. of plasma or serum in a 15-ml. centrifuge tube, which is then shaken, incubated at 38° C. for 30 minutes and centrifuged at high speed for 15 minutes. The supernatant plasma is treated with 8 volumes of acid cadmium sulphate reagent (13·0 g. of pure hydrated cadmium sulphate and 63·5 ml. of exactly *N* sulphuric acid made up to 1 litre with water) followed by 1 volume of 1·1 *N* sodium hydroxide solution. The mixture is shaken, allowed to stand for 15 minutes and filtered, and the filtrate is diluted, if necessary, so as to contain 2 to 12γ of inulin per ml. Five ml. of diluted urine (which usually does not need to be fermented) or of the filtrate from plasma or serum are transferred to a thick-walled test-tube (20 × 110 mm.), and 10 ml. of diphenylamine reagent are added. (The reagent is made by mixing 12 volumes of a 10 per cent. solution of pure diphenylamine in redistilled absolute alcohol with 192 volumes of a mixture of 80 volumes of conc. hydrochloric acid and 112 volumes of redistilled absolute alcohol. The solution does not keep for more than a week.) The tubes are tightly stoppered, immersed in a boiling water-bath for exactly 60 minutes and then plunged into cold water. The colour of the resulting solution is measured in a photometer. The Evelyn photo-electric colorimeter with a No. 660 filter proved most satisfactory, but the Zeiss–Pulfrich "Stufenphotometer" and the Dubosq colorimeter have also been used. A blank determination with distilled water is made at the same time, and the instrument is calibrated by measuring the colour given by solutions of inulin of known strength. The method was used to estimate the glomerular filtration rate, and a correction had to be applied for the small amount of colour produced by blood and urine containing no inulin. Inulin added to plasma or serum in amounts varying from 4 to 15 mg. per 100 ml. was determined with an error of 2 per cent. or less, and equally accurate results were obtained with plasma and urine from patients suffering from severe uremia or severe jaundice and with urines containing large quantities of protein. Good results were also obtained with the plasma and urine from diabetic patients, but for these fluids the fermentation technique had invariably to be employed. F. A. R.

Studies on the Nature of the Iodine in Blood. V. Trevorrow. (*J. Biol. Chem.*, 1939, **127**, 737–750.)—The iodine-contents of numerous fractions prepared from whole blood or blood plasma were estimated by the method of Trevorrow and Fashena (*J. Biol. Chem.*, 1935, **110**, 29; 1936, **114**, 351; Abst., ANALYST, 1935, **60**, 628). It was found that all the iodine present in blood could be extracted with boiling alcohol or cold acetone; added potassium iodide and thyroxine were extracted quantitatively with either solvent, but the iodine of added thyroid gland could not be extracted with alcohol. It was concluded from these experiments that blood iodine is not present in protein combination. Attempts to remove iodine from the plasma proteins by ultra-filtration were to a large extent unsuccessful, for only 10 to 20 per cent. of the iodine was present in the filtrate. It was found, however, that thyroxine added to the plasma also did not pass through collodion membrane, but that added potassium iodide did; this suggested that not more than 20 per cent. of the plasma iodine is in inorganic combination. This conclusion was confirmed by the observation that most of the iodine was precipitated with the proteins on heating with acetic acid or on treatment with zinc sulphate and sodium hydroxide solutions, and that added thyroxine (but not added potassium iodide) was likewise precipitated. It therefore appears that the iodine in blood is present in the form of a compound closely resembling thyroxine, and this hypothesis is supported by the fact that all the iodine in blood can be extracted with butyl alcohol. However, whilst thyroxine remains wholly in the butyl alcohol layer when this is shaken with sodium hydroxide solution, the iodine from blood is partitioned between the two phases. Di-iodotyrosine, on the other hand, is completely extracted by alkali. The exact nature of the iodine-containing compounds in blood has not yet been established with certainty. F. A. R.

Purification and Some Properties of Renin. O. M. Helmer and I. H. Page. (*J. Biol. Chem.*, 1939, **127**, 757–763.)—An active extract of the pressor substance of pig kidney cortex was prepared by extraction of the acetone-dried gland with sodium chloride solution. This solution was acidified to *p*H 4·5 and, after removal of the inert proteins, the active principle was precipitated by adding sodium phosphate solution to the filtrate. The precipitate was extracted with sodium chloride solution acidified with acetic acid, and the filtrate was dialysed and freed from inert protein by adding alkali to *p*H 6·5. The resulting product contained 0·4 mg. of nitrogen per ml. It has strong pressor activity, as had also a picrate and a reineckate prepared from it. The active principle was precipitated by ammonium sulphate at 40 per cent. concentration and by sodium chloride at full concentration, both at *p*H 3 to 4. The solution was inactivated by heating it above 56° C. Positive reactions were obtained for guanidine groups and for pentose, but a test for adrenine was negative. The most active fraction prepared caused a rise of 30 mm. in the arterial blood pressure of a dog when injected in quantities representing 0·027 mg. of nitrogen per kg. of body-weight. In cats, 0·009 mg. of renin nitrogen produced a rise of 32 mm. The evidence so far available suggests that the pressor substance is not adrenine. F. A. R.

Colorimetric Reaction for the Quantitative Estimation of Nicotinic Acid. E. Bandier and J. Hald. (*Biochem. J.*, 1939, 33, 264–271.)—Nicotinic acid, metol (*p*-methylaminophenol sulphate) and cyanogen bromide in aqueous solution give a yellow solution, the colour of which is stable and proportional to the amount of nicotinic acid present. A measured amount (up to 9 ml.) of the aqueous solution to be tested, containing 0·005 to 0·25 mg. of nicotinic acid, is run into a graduated 20-ml. flask, which is then heated for 5 minutes on a water-bath at 75° to 80° C. One ml. of a freshly-prepared 4 per cent. aqueous cyanogen bromide solution is added, and the mixture is placed on the water-bath for another 5 minutes and then cooled to room temperature. (A 5 per cent. solution of cyanogen bromide can readily be made by adding potassium cyanide to a saturated aqueous solution of bromine until the latter is just decolorised.) Ten ml. of a freshly-prepared solution (about 5 per cent.) of metol are added, and the solution is made up to 20 ml. with water. After the mixture has stood for 1 hour at room temperature excluded from light, the intensity of the colour is measured in a Pulfrich photometer (filter S43) with a blank solution containing cyanogen bromide and metol in the other cell. When the amount of nicotinic acid taken is in excess of 0·25 mg., it is futile to dilute the final coloured solution; the original solution must be diluted and the determination repeated. A calibration curve with known amounts of nicotinic acid is constructed. Nicotinamide also gives a yellow colour, but this is considerably stronger than with nicotinic acid, so that when the amide and the acid occur together, it is better to hydrolyse the solution before carrying out the estimation. Nicotinic acid can be determined in biological material, for example in yeast, by the following procedure:—Ten ml. of 2 *N* sodium hydroxide solution are run into a 20-ml. graduated flask, 5 g. of dry yeast are added, and the neck of the flask is closed with a wad of non-absorbent cotton-wool. The flask is shaken, placed on a boiling water-bath for 30 minutes and allowed to cool, and 1·8 ml. of conc. (36 per cent.) hydrochloric acid are introduced, drop by drop, with shaking. The solution, which now has a *p*H of 4 to 6, is diluted to 20 ml. with water. The contents are thoroughly mixed, a portion is centrifuged, exactly 1 ml. (equivalent to 250 mg. of yeast) is transferred to a second centrifuge tube, and 9 ml. of acetone are slowly added from a burette. The tube is closed with a rubber stopper, shaken for a few minutes and centrifuged, whereby a very small (about 0·3 ml.) aqueous layer and a nearly colourless layer of aqueous acetone are formed. Three ml. of the acetone layer (equivalent to 75 mg. of yeast) are mixed with 3 ml. of water in a round-bottomed flask, and the acetone is removed at room temperature by means of a water vacuum-pump. The residual aqueous solution is quantitatively transferred with the aid of *N*/15 potassium acid phosphate solution to a 20 ml. graduated flask. The rest of the procedure is the same as that described above. Quantitative recoveries of added nicotinic acid were obtained by this method.

F. A. R.

Determination of Cholesterol by Chromic Oxidation. F. Kayser and C. Mathieu. (*Bull. Soc. Chim.*, 1939, **6**, 715–717.)—The method depends on the complete oxidation of the digitonin-cholesterol complex by means of potassium dichromate in presence of silver nitrate as catalyst. The recommended procedure is as follows:—The digitonin-cholesterol precipitate (about 1 g.) is collected on a Jena glass filter and the filter is transferred to a flask carrying a ground reflux column. Twenty ml. of 0·05 *N* chromic mixture (500 ml. of 0·1 *N* aqueous potassium dichromate solution with sulphuric acid to 1 litre) and 0·2 ml. of 25 per cent. silver nitrate solution are added. The liquid is heated on an oil-bath and kept at the boiling-point for 40 minutes. After cooling, a little water is added, and the liquid is transferred to a 200-ml. graduated flask, treated with 0·4 ml. of 5 per cent. sodium chloride solution and made up to 200 ml. An aliquot portion is filtered through a Jena glass filter, and 20 ml. of the filtrate are treated with 20 ml. of water (the analysis must be carried out in a normal acid solution) and a crystal of potassium iodide, and titrated with 0·02 *N* sodium thiosulphate solution, starch being used as an indicator. The complete oxidation of 1 mg. of cholesterol requires 0·3938 ml. of *N* dichromate solution, and the oxidation of the digitonin-cholesterol complex requires 0·254 ml. E. M. P.

Potentiometric Titration of Carotenoids with Gold Trichloride Solution. P. Karrer and W. Jaeger. (*Helv. Chim. Acta*, 1939, **22**, 314–322.)—In a previous paper (*cf.* ANALYST, 1938, **63**, 835) attention was directed to the error introduced by the presence of carotenoids in the estimation of tocopherol by titration with gold chloride solution. The oxidation of several carotenoids by this reagent has now been studied quantitatively. The carotenoids were dissolved in a small amount of ether, and the solution was diluted with 5 to 10 times its volume of alcohol and titrated with 0·01 *N* aqueous gold chloride solution at 65° to 75° C., the time required varying from 140 to 345 minutes. It was found that α- and β-carotene, lycopene, xanthophyll and zeaxanthin required 8 equivalents of gold chloride. Astacene and rhodoxanthin required 2 equivalents. Crocetin, bixin, fucoxanthin and violaxanthin were not oxidised. F. A. R.

Conversion of Carotene into Vitamin A_2 by some Fresh-water Fishes. R. A. Morton and R. H. Creed. (*Biochem. J.*, 1939, **33**, 318–324.)—Perch (*Perca fluviatilis*) were successfully maintained in captivity on a diet of blow-fly larvae, and these fish were used to determine whether carotene is a provitamin A and provitamin A_2. The fish were divided into two groups, one receiving blow-fly larvae only, the other being given the larvae coated with powdered carotene. After two months the fish were killed, and the amounts of vitamins A and A_2 present in various organs were determined by spectroscopic examination of the blue solution formed by adding antimony trichloride solution to the unsaponifiable fraction. The vitamin A content of the livers of the fish that had received carotene was twice as high as that of the control group and the amount of vitamin A_2 was three times as great. Even so, however, the storage levels of the fish receiving carotene was not raised to that of larger fish feeding naturally, and it would appear that, whilst carotene is both a provitamin A and a provitamin A_2, it is not the only provitamin. The amount of carotene in zooplankton, such as constitute the diet of perch, was found to be relatively small. Dace also were fed on blow-fly larvae with and without added carotene, and estimations of the vitamin contents of various organs indicated a substantial increase in the amount of both vitamins as a result of adding carotene to the diet. F. A. R.

Distribution of Vitamins A and A_2. II. J. A. Lovern, R. A. Morton and J. Ireland. (*Biochem. J.*, 1939, **33**, 325–329.)—In continuation of the work previously described (*cf.* ANALYST, 1938, **63**, 358) other species of fish have now been examined. A large sturgeon (*Acipenser sturio*) yielded 1·47 kg. of liver oil containing 1 per cent. of vitamin A, and part of the intestines gave 29·3 g. of oil containing 10 per cent. of vitamin A. The liver contained 30 g. of vitamin A esters and 7 g. of vitamin A_2 esters, and the intestines 6 g. and 0·5 g. of vitamin A and vitamin A_2 esters respectively. The ratio vitamin A/A_2 was much higher in the intestines than in the liver, as was also found with salmon, trout and halibut. Lamperns (*Petromyzon fluviatilis*) contained little vitamin A, although it was present at a number of sites, and even less vitamin A_2. Dogfish (*Squalus acanthias*) gave a liver-oil poor in vitamin A, and the intestines also contained only a small amount. It is suggested that the dogfish and some other species do not utilise vitamin A in fat absorption to the same extent, for instance, as the halibut, cod and salmon. The herring-gull (*Larus argentatus*), the skua (*Megalistris catarrhactis*) and the gannet (*Sula bassana*) were found to contain more vitamin A in their intestines than such animals as the rabbit; no vitamin A_2 was detected in any of the organs of these sea-birds. The one gannet that was examined contained quite large amounts of vitamin A in the lungs.

A preliminary study was also made of the provitamin D contents of sterols from different sources. Cholesterol from cod-liver oil, salmon-liver oil and similar sources contained 0·03 to 0·1 per cent. of provitamin D, but the sterol from halibut stomach contained about 0·5 per cent. The sterol from halibut spleen showed a broad absorption band at 275 $m\mu$ due to an unknown substance that was absent from the spleen sterols of bullock (0·02 per cent. of provitamin D) and sheep (0·06 per cent.). F. A. R.

Distribution of Vitamins A and A_2. III. J. A. Lovern and R. A. Morton. (*Biochem. J.*, 1939, 33, 330–337.)—Preliminary experiments were made to determine the distribution of vitamins A and A_2 in the different layers of halibut intestine. From the lumen to the outer wall, these layers are as follows:—(1) *Mucosa,* (*a*) *epithelium,* (*b*) *tunica propria,* (*c*) *stratum compactum* and (*d*) *stratum granulosum.* (2) *Muscularis* (*a*) *circularis and* (*b*) *longitudinalis.* (3) *Serosa* (*a*) *serosa* proper and (*b*) *sub-serosa.* Two methods were investigated. In the first, a hand-cut section, 1 to 2 mm. thick, of the fresh intestine was cleared by immersion in a homogeneous mixture of glucose and golden syrup and a photomicrograph was made with a "Pointolite" bulb as illuminant. A second photomicrograph was then made with a sheet of Wood's glass placed between the light source and the microscope (with, of course, a longer exposure), so that only ultra-violet light was utilised. Comparison of the two photographs showed that the mucosal coats were much more opaque to ultra-violet light than to visible light, whilst the muscle layers showed little sign of such selective absorption.

A better method of investigating the distribution of the vitamins in the different layers is to separate them mechanically, and to estimate the vitamin-contents in each layer by the usual procedure. The *tunica propria* was found to be far richer in vitamin A than the other mucosal coats, whilst these in turn were much richer than the muscle and *serosa.* The distribution of fat was similar to that of the vitamin A. The mechanism of fat absorption in fishes is different from that obtaining in mammals, proceeding directly through the mucosal epithelium and not by a lymphatic system. The *stratum compactum* forms a barrier to the transport of fat as droplets which accumulate in the adjacent *tunica propria,* and the hypothesis is advanced that vitamin A esters in combination with protein may be instrumental in transporting these droplets from the *tunica propria.* F. A. R.

Halibut Intestinal Oil. J. A. Lovern, T. H. Mead and R. A. Morton. (*Biochem. J.*, 1939, 33, 338–343.)—A sample of the oil from fresh halibut intestine was subjected to molecular distillation, Hickman's constant-yield oil (*J. Ind. Eng.*

Chem., 1937, **29**, 1107) being used. It was thus shown to contain 95 per cent. of its vitamin A in the form of esters. Oil from halibut intestines that were a few days old was found to contain a high proportion of free fatty acid, and 20 to 30 per cent. of the vitamin existed in the free state. The presence of the fatty acids facilitated cyclisation of the vitamin. Oil from autolysed halibut intestines contained about 25 per cent. of material that was not glyceride, vitamin ester or sterol ester, and a fraction soluble in water that exhibited selective absorption at 261 $m\mu$. The elimination curve of vitamin A_2 closely resembled that of vitamin A.

F. A. R.

Occurrence of Vitamin B_2 (Lactoflavin). II. Vitamin B_2 in Animal Organs. J. Schormüller. (*Z. Unters. Lebensm.*, 1939, **77**, 346–357.)—In continuation of the investigation of the occurrence of vitamin B_2 (*Z. Unters. Lebensm.*, 1939, **77**, 1; Abst., ANALYST, 1939, **64**, 215), the lactoflavin-content of different animal organs has been determined by the methods previously described. The results for the organs of recently killed cattle (γ per 100 g. of dry material) were as follows:—liver, 5550 to 7410; kidney, 6170; lung, 2220; heart, 1750; spleen, 1090. Corresponding figures for the organs of the edible mussel were:—liver, 1763; heart, 645. In order to investigate the degree of combination of the lactoflavin with the colloidal carrier (yellow enzyme) the flavin bodies were extracted with solvents and separated into their high-molecular and low-molecular components by dialysis in the manner previously described (*loc. cit.*). By extraction of ox-liver with cold water, it was found that 88·1 per cent. of the extracted lactoflavin is combined with the colloidal carrier. By extraction of pulped liver with water at 37° C., 31·3 per cent. of the total flavin present was extracted, and this figure was increased to 41·07 per cent. when the liver was ground after preliminary treatment with liquid air. By extraction of liver with various solvents it was shown that the amount of flavin extracted varied with the solvent used, the greatest amount being obtained by the use of anhydrous glycerin. By incubation of pulped liver with water at 37° C. and periodic analysis of the extracted flavins it was shown that no measurable destruction of the vitamin occurred, but that it was separated from the colloidal carrier in progressively increasing amounts. It therefore appears that there is no danger of loss of the vitamin by autolysis during the storage of the liver. Investigation of the flavin-content of different parts of the kidney of the horse showed that the lactoflavin-content varied in parts of the same organ which are structurally and functionally different. Similar determinations of the lactoflavin-content of different portions of the heart of the horse showed that, as in muscle, an inverse relationship exists between the lactoflavin-content and the glycogen-content. Other physiological relationships are discussed.

A. O. J.

Separation of Lactoflavin and Lactoflavin Phosphate. A. Emmerie. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 290–292.)—Lactoflavin can be extracted from aqueous solution by benzyl alcohol and other aromatic alcohols, whereas only traces of lactoflavin phosphate are thereby extracted. Thus 76 per cent. of the lactoflavin was found to be present in the benzyl alcohol phase when equal volumes of the alcohol and water (*p*H 5 to 7) were shaken and allowed to separate.

The determination of lactoflavin and lactoflavin phosphate was made by measuring the intensity of the colour in a Zeiss-Pulfrich photometer. The procedure recommended for determining the amount of free and combined flavin in urine is to prepare an extract as previously described (*Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, 1936, **6**, 136), and evaporate the eluate from the lead sulphide to dryness under reduced pressure. The residue is taken up in water, and the solution is oxidised with potassium permanganate and hydrogen peroxide in acetic acid solution, and then neutralised and shaken with benzyl alcohol. The difference between the intensity of the colour of the aqueous extract before and after benzyl alcohol extraction is equivalent to the amount of lactoflavin present, whilst the colour of the aqueous extract after the extraction is due to lactoflavin phosphate. F. A. R.

Colorimetric Estimation of Tocopherol (Vitamin E). II. Adsorption Experiments. A. Emmerie and C. Engel. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 283–289.)—Tocopherol can be separated from carotenoids and vitamin A by chromatographing a benzene solution (5 ml.) on a column (30 × 12 mm.) of "Floridin XS" earth, which has been purified by digestion with hot conc. hydrochloric acid, and washed with water, alcohol and benzene. The chromatogram is developed with 25 ml. of benzene, which is sufficient to wash the tocopherol quantitatively through the column into the filtrate. The carotenoids and vitamin A are retained on the adsorbent. Wheat-germ oil is freed from carotenoids and rendered quite colourless by this treatment. Alumina retains tocopherol as well as carotenoids and vitamin A from petroleum spirit, and the tocopherol is quantitatively eluted by methyl alcohol. A vitamin A concentrate treated with the ferric chloride—dipyridyl reagent used for estimating tocopherol (*cf.* ANALYST, 1939, **64**, 216), slowly loses its activity as a result of oxidation by the reagent. The reaction takes much longer, however, to reach the end-point both with vitamin A and with carotene than with tocopherol. F. A. R.

Bacteriological

The Methylene Blue Reduction Test and the Keeping Quality of Milk. C. H. Chalmers. (*J. Dairy Res.*, 1938, **9**, 351–355; *Bull. Hyg.*, 1939, **14**, 333.)—In view of the poor correlation of the methylene blue test with the keeping quality of milk under conditions prescribed in Memorandum No. 139 of the Ministry of Health (Special Designations) Order, 1936, the author carried out a series of tests with milk, holding it for varying periods of time at 15° C. before submitting it to the test. The milk was produced at 7.0 a.m., cooled at the farm, collected at 10.0 a.m. and taken immediately to the laboratory. Two hundred samples were examined, and each was divided into six portions which were held at 15° C. for periods of time ranging from 1 hour to 23 hours. The portions examined after 1 hour at 15° C. showed very poor correspondence between reduction time and keeping quality, and the correspondence was little better after 7 hours. The portions kept for 16 hours at 15° C. showed better, though not very good, correlation, whereas with those held for 23 hours the correlation was fairly close. The author suggests that during the time in which the milk is kept before being tested the species of organisms change progressively, so that the predominant type at any one time differs from that at any other. D. R. W.

Water

Quantity of Zinc in Sea Water. G. Bertrand. (*Bull. Soc. Chim.*, **1939**, **6**, 697–700.)—The following method was used for the determination of zinc in water from the Channel or the Atlantic Ocean:—One litre of sea water was evaporated to a quarter of its volume in a porcelain dish after addition of 1 ml. of pure conc. hydrochloric acid. A slight excess of 20 per cent. barium chloride solution (about 35 ml.) was added gradually to precipitate the sulphates, and the liquid was treated, without filtering, with about 10 drops of perhydrol, 40 ml. of pure ammonia, free from carbonate, and then gradually with pure lime to displace the magnesium. With water from the Mediterranean, which has a higher salt-content, the volume was reduced to a third after addition of 2 ml. of hydrochloric acid, and 50 ml. of ammonia were used. The precipitate was separated by centrifuging, and the solution was transferred to a conical flask. The basic constituents of the precipitate were dissolved in the minimum quantity of pure hydrochloric acid, the liquid was diluted to about 250 or 300 ml., and the precipitation with ammonia and a little lime was repeated. After centrifuging, the liquid was added to the first one. For greater accuracy a second and, if necessary, a third treatment with acid and alkali was made. The liquid finally obtained was analysed by the method of Bertrand, Bertrand and Javillier, and Bertrand and Mokragnatz (*Comptes rend.*, 1892, **115**, 939, 1028; *Bull. Soc. Chim.*, **1906**, **1**, **63**; **1923**, **33**, 1539), the zinc being weighed as the anhydrous sulphate. With water from the Dead Sea, 250 ml. of the water diluted with an equal volume of pure water were taken for the analysis. The following results were obtained:

Sea water	Volume of water litres	Zinc sulphate mg.	Zinc, mg.	Zinc, g. per cubic metre
North Sea ..	2	15·3	6·197	3·10
Channel	1	8·5	3·442	3·44
Channel	3	27·0	10·935	3·65
Atlantic Ocean ..	2	15·2	6·156	3·08
Mediterranean ..	2	18·7	7·573	3·79
Dead Sea ..	0·25	2·7	1·094	4·37

E. M. P.

Organic

Rapid Method of Determining Water in Butyl Alcohol. G. Lazzari. (*Chim. e Ind.*, **1939**, **21**, 68–69.)—The method depends on the turbidity produced when butyl alcohol containing water is treated with a mixture of 2 volumes of pure benzene and 1 volume of pure acetone (rectified at 56° C.). The recommended procedure is as follows:—Twenty ml. of the butyl alcohol under examination and 2 ml. of the benzene-acetone mixture are pipetted into a 50-ml. flask of colourless glass with a tightly fitting stopper. Water is added dropwise from a burette graduated in twentieths of a ml., and after each addition the flask is stoppered and shaken vigorously for a few seconds. The reading is taken when the liquid shows a persistent opalescence. Too vigorous shaking appears to destroy the emulsion, possibly by raising the temperature, but if the liquid is allowed to stand at the temperature of the experiment the turbidity reappears. The addition of 0·025 ml. of water in excess gives a definite opalescence, so that the end-point can be accurately determined. By using a micro-burette and observing the turbidity in a nephelometer, very accurate results can be obtained. For ordinary work, such as the determination of water in butyl alcohol which is to be used for dehydrating organic substances, it may be of assistance to use a device such as observing in diffuse daylight writing placed 15 cm. behind the flask and taking as the end-point the point at which the writing cannot be deciphered. The water-content, when the temperature is 16° C., can be calculated from the equation

$$\text{Volume per cent. of water} = -4{\cdot}27n + 15{\cdot}8,$$

where n is the volume of water added, in ml. For temperatures not far removed from 16° C., the relation is

$$\text{Volume per cent. of water} = -4{\cdot}27n + 15{\cdot}8 + 0{\cdot}07(t - 16),$$

where t is the temperature. E. M. P.

Behenic Acid in the Seed Oil of *Pongamia glabra*, Vent. B. L. Manjunath and M. S. Shankara Rao. (*J. Indian Chem. Soc.*, 1938, **15**, 653.)—The crude oil obtained from the seeds of *Pongamia glabra* (Hongey in Kannada, Karanja and Naktamala in Sanskrit and Sukchain in Hindi) gradually forms a solid deposit after standing for several days. This deposit was repeatedly washed with methyl alcohol to remove resins, and after all the karanjin had been extracted (Beal and Katti, *Zentrbl.*, 1926, **2**, 596; Limaye, *Proc. Indian Sci. Congress*, 1925, **1**, 18), the fatty acids in the residue were liberated and their methyl esters were distilled under reduced pressure (0·5 mm.). From the first of the two chief fractions (b.p. 199–205° C. at 0·5 mm.) behenic acid (m.p. 78°–79° C.) was liberated and purified by repeated crystallisation from methyl alcohol. The free acid of the second fraction (b.p. 207–212° C. at 0·5 mm.) and residue appeared to consist of lignoceric acid. Since behenic acid was not found by Sudborough *et al.* (*J. Indian Inst. Sci.*, 1923, **6**, 93) in the refined oil, it is probably removed during the refining process. D. G. H.

Oil of *Aleurites trisperma*. E. D. G. Frahm and D. R. Koolhaas. (*Rec. Trav. Chim. Pays-Bas*, 1939 **58**, 277–282.)—The oil from an authentic specimen of *Aleurites trisperma* had the following constants: sp. gr. at 15·5°/15·5° C., 0·9344; n_{D}^{25}, 1·4980; acid value, 4·9; saponification value, 190·8; Reichert-Meissl value, 0·61; hexabromide value, 0; iodine value (Wijs), 133·1; iodine value (Rosenmund-Kuhnhenn), 127·6; diene number (Ellis and Jones), 43·2; unsaponifiable matter, 0·5 per cent.; total fatty acids, 93·1 per cent.; saturated fatty acids (Bertram), 17·0 per cent. From the diene number it was computed that the oil contained 47·3 per cent. of elaeostearic acid, but this amount was not sufficient to account for the iodine value found, and it was suspected that an unsaturated acid other than elaeostearic and oleic acids was present. A portion of the fatty acids was therefore treated with ozone, and the oxidation product was steam-distilled. The volatile acids were fractionated and shown to consist of *n*-valeric and caproic acids, identified as anilides, and pelargonic acid, identified as its zinc salt. Azelaic acid was identified in the non-volatile portion. Oxidation of the fatty acids with alkaline potassium permanganate solution similarly gave a mixture, in which *n*-valeric acid, caproic acid, pelargonic acid and 9 : 10-dihydroxystearic acid were identified. The presence of pelargonic acid among the oxidation products suggested that 9:12-linolic acid was present in the original oil, a suspicion that was confirmed by the identification of sativic acid (m.p. 174° C.) among the products obtained by more cautious oxidation with an excess of potassium permanganate amounting to not more than 10 per cent. of the amount calculated from the diene number and iodine value. This method has also been used to detect linolic acid in other oils, *e.g.* the oil of *Parinarium corymbosum*. Further calculations, based on the iodine value of linolic acid, indicated that the oil contained 18·0 per cent. of linolic acid and 10·8 per cent. of oleic acid, and the mean molecular weight of the saturated acids indicated that the amounts of palmitic acid and stearic acid present (only these could be detected) were 9·1 per cent. and 7·9 per cent. respectively. Thus the composition of the oil of *Aleurites trisperma* may be represented as: elaeostearin, 49·4; linolin, 18·8; olein, 11·3; palmitin, 9·5; stearin, 8·3; unsaponifiable matter, 0·5 per cent. These values differ widely from those previously reported by Jamieson and McKinney (*Oil and Soap*, 1935, **12**, 146). F. A. R.

Drying Oil of *Licania crassifolia* Benth. M. Sesseler and P. A. Rowaan. (*Chem. Weekblad*, 1939, **36**, 208–209.)—In the course of investigations into a substitute for Chinese wood oil, experiments were made with oils related to oiticica oil (from the seeds of *Licania rigida* Benth.) and obtained from the seeds of the plants *L. heteromorpha* Benth. ("japoballi") and *L. macrophylla* Klotzsch ("sponsehoedoe") which occur in Surinam (Dutch West Indies). These yielded only 0·5 to 1·0 per cent. of an oil soluble in petroleum spirit, and are considered of little interest. The seeds of *L. crassifolia* Benth. ("kwepilan"), however, gave a yield of 5 per cent. of oil by the expression method and 25 per cent. by extraction with petroleum spirit. They are pear-shaped, and have an average length of 10 mm. and an average thickness at the thickest part of 5 mm., and the endosperm contains about 60 per cent. of oil. Analytical data for the expressed and extracted oils, respectively, were as follows:—sp.gr. (15°/15° C.), 0·9588, 0·9555; n_D^{20}, 1·5367, 1·5292; acid value, 1·3, 2·9; saponification value, 191·5, 189·2; unsaponifiable matter, 1·3, 1·4 per cent.; saturated acids (Bertram), —, 7·1 per cent.; iodine value (Wijs, 1 hour), 163·2, 164·7; thiocyanogen value (24 hours), —, 118·8; diene value, 69·5, 71·0; carbonyl value (Leithe, *Fette Seifen*, 1938, **45**, 615), —, 105·0. The mean mol. equiv. of the fatty acids was 278, and the acids contained 18-C-atoms. The "heating-test" (*Proc. Amer. Soc. Testing Materials*, 1935, **35**, Part 1, 1397) showed that the oil formed a hard jelly after 9 minutes at 293° C., compared with 10·75 minutes for a "standard sample American tung oil" (maximum permissible value, 12 minutes). Analytical data for the separated fatty acids were:—iodine value (Wijs), 177·0; thiocyanogen value, 90·8; diene value, 63·2; hexabromide test, negative; these are in line with the gelatinising properties of the oil. The unsaturated acids were investigated (after C. P. A. Kappelmeier, *Fettchem. Umschau*, 1935, **42**, 145) by saponification of the oil for 1 hour with a solution of sodium hydroxide in alcohol, followed by removal of the alcohol by distillation and precipitation of the fatty acids from a solution of the soap in water. The mixture was then extracted with benzene, and the extract was dried with anhydrous sodium sulphate, evaporated to a small volume, and left to crystallise in sunlight. After recrystallisation from acetone the m.p. of the resulting crystals was 91° C., but it was not possible to prepare a satisfactory specimen of the semicarbazone owing to the insolubility and sticky nature of the specimen. Extraction of the acids with ether or petroleum spirit, however (*cf.* Brown and Farmer, ANALYST, 1935, **60**, 570), and evaporation of the dehydrated extract in a vacuum, gave crystals (m.p. 75° C.), which were less sticky; whilst the use of carbon tetrachloride (*cf.* Steger and Van Loon, *Rec. Trav. Chim. Pays Bas*, 1938, **57**, 6) gave a dark red-brown solution containing a sticky residue, which deposited crystals with m.p. 95° C. The m.p. of the corresponding semicarbazone was 137° C., and the acid value was 188·4 (theoretical value for licanic acid, 191·7). The remainder of the sticky residue was recrystallised from petroleum spirit and then had m.p. 94° to 98° C. It is concluded that the glycerides of the oil are derived from the following acids:—licanic, approx. 60; linolic, approx. 20; oleic, approx. 5; saturated acids, 7 per cent. J. G.

Antioxygens in Natural Fats. IV. The Proportions and Properties of Antioxygenic Compounds in Various Extracted Seed Cakes. T. P. Hilditch and S. Paul. (*J. Soc. Chem. Ind.*, 1939, 58, 21–24.)—The antioxygenic activities and other properties of palm-kernel, linseed, soya-bean, arachis and cotton-seed meals have been examined. The meals were prepared as described previously (*J. Soc. Chem. Ind.*, 1937, **56**, 23T; Abst., ANALYST, 1937, **62**, 206). The final yields of acetone-soluble concentrates were of the same order as before, establishing the same order for all the meals. The times in the oxidation tests, in hours, for the meals were, respectively:—palm-kernel, 5; linseed, 5; soya-bean, 14; arachis, 12; cotton-seed, 27. In each instance a small proportion of nitrogen was present in the concentrate; but, although there is a slightly closer parallelism between the nitrogen-contents and antioxygenic activities than between the degree of unsaturation and antioxygenic activities, it is not well marked. Almost complete suppression of activity occurs when an acetone solution of the original concentrate is exposed to a few bubbles of dry hydrogen chloride gas. With regard to the chemical nature of the natural antioxygenic compounds in seed meals, it is established that they show marked reducing power, which suggests the presence of reducing carbohydrates; ferric chloride solution gives a light brown colour; they contain 0·4 to 1·0 per cent. of combined phosphorus and 1 to 2 per cent. of combined nitrogen, and their antioxygenic properties disappear on prolonged heating with water or immediately on exposure to traces of hydrogen chloride; with the latter these properties are partly restored on subsequent careful neutralisation of the acid. The authors believe that they have established the fact that seeds contain natural antioxygenic compounds characterised by their basic or pseudo-basic nature. Although the identity of the basic component was not determinable, there is some reason to think that basic oxygen, rather than basic nitrogen, may be the responsible factor for retardation of atmospheric oxidation. D. G. H.

Lignin and Related Compounds. The Ethanolysis of Spruce, Maple and other Woods. L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert. (*J. Amer. Chem. Soc.*, **1939**, **61**, 868–869.)—Water-soluble ethanolysis products are isolated from various woods in higher yields and in purer condition than by the method previously described (Cramer, Hunter and Hibbert, *J. Amer. Chem. Soc.*, **1939**, **61**, 523). In the new method the final extraction is made with benzene in an atmosphere of carbon dioxide. The wood meal (40-mesh) is air-dried and extracted for 48 hours with a 1:1 mixture of absolute ethanol and benzene and then for 24 hours with absolute ethanol, after which it is washed with hot running water for 12 hours, and dried first in the air and afterwards in a vacuum oven (20 mm. pressure) for 48 hours. For the ethanolysis the wood meal (1000 g.) is heated under reflux for 48 hours with dry ethanol (8 litres) containing anhydrous hydrogen chloride (160 g.) in an atmosphere of carbon dioxide. The mixture is cooled and filtered, and the residual meal is washed with hot ethanol. The combined ethanol extracts are concentrated under reduced pressure at 50° C. and dropped in a very fine stream into water which is being vigorously stirred. The precipitated ethanol lignin is filtered off and well washed. The aqueous solution and washings are concentrated, and the solution is extracted for 48 hours with benzene. The precipitated ethanol lignin is shaken five times with benzene for at least 2 hours each time to remove adsorbed oils, and the benzene extract is treated separately. The oils isolated from each portion are fractionated separately. In typical determinations the total oils extracted (expressed as per cent. on the weight of Klason lignin in the original material) were as follows:—spruce, (1) 10·9; (2) 14·2; maple, (1) 33·5, (2) 35·4; Douglas fir, 14·6; redwood, 13·9; red oak, 50·9; bamboo, 50·1; jute, 74·0; maize stalks, 59·6; rye straw, 40·6. The preliminary results indicate that the ethanolysis method is broadly suitable for isolating in high yields the constructional units from the lignin of a wide variety of plant types. D. G. H.

Combination of Formaldehyde with Collagen. J. H. Highberger and C. E. Retzsch. (*J. Amer. Leather Chem. Assoc.*, **1939**, **34**, 131–148.)—The study of the combination of formaldehyde with collagen has been seriously hampered in the past by the lack of a method for the accurate determination of the amount of formaldehyde present in the tanned leather. The authors' method (ANALYST, **1938**, **63**, 678) has, therefore, been used for this purpose, the experimental material being 2·0 g. of a purified collagen powder prepared from fresh, dry, ash-free steer hide (*cf. J. Amer. Leather Chem. Assoc.*, **1936**, **31**, 93). This was tanned in 100 ml. of a 0·1 *N* solution of a phosphate buffer, to which were added sufficient 0·1 *N* sodium hydroxide solution to bring it to a desired *p*H (*i.e.* equivalent to 4 to 11 after the tanning process), and sufficient of a standardised 10 per cent. solution of formaldehyde to bring the concentration of this substance to 0·25 to 3·0 g. per 100 ml. The experiments were made within 1 or 2 hours of the preparation of the mixture in order to eliminate any reduction in the true concentration of the formaldehyde owing to the occurrence of the Cannizzaro reaction; this is particularly important when the alkaline range is used. The tanning-period was normally 24 hours, and during this time the mixtures were agitated continuously in a shaking-machine. After the tanning the *p*H was determined by means of the glass electrode, and the tanned powders were washed over-night under standardised conditions with 15 to 19 litres of distilled water. A modification of the Schiff test (sensitiveness, 1:10,000) was then used to confirm the absence of free formaldehyde in the wash water, and the amount of formaldehyde in the tanned powder was finally determined by the authors' method (*loc. cit.*). Curves show the number of mg.-mols. of formaldehyde fixed per g. of collagen plotted against the tanning-time (up to 24 hours), the concentration of formaldehyde, and the *p*H, and the following conclusions are drawn:—When the concentration of formaldehyde is 1 per cent. or less, the reaction is confined to the free amino and guanidino groups provided by lysine and arginine, respectively, and one mol. of the formaldehyde reacts with each amino or guanidino group. Within this concentration range only the amino groups of lysine react at *p*H values of 8 or less, but above *p*H 8 the guanidino groups of arginine are involved. The data showing the effects of the tanning-time on the final *p*H indicate that a *p*H-equilibrium is established by the end of the first hour, although the fixation of formaldehyde continues to increase markedly throughout the first 8 hours. This suggests that the reaction is not ionic but molecular in nature, since it proceeds more slowly than would be expected of an ionic reaction. This is confirmed by the other results, which indicate that only un-ionised basic groups participate in the reaction. It follows that the function of the alkaline reaction in promoting formaldehyde tannage is to repress the ionisation of the basic groups. When the concentration of formaldehyde exceeds 1 per cent. it is fixed in larger quantities, and it is suggested that this may be due either to the extension of the reaction to the imino groups of the protein "back-bone," or to the reaction of the groups mentioned above with polymerised molecules of formaldehyde, or to both causes. This work fails to confirm the analogy which some workers (*e.g.* Küntzel, *angew. Chem.*, 1937, **50**, **308**) have drawn between urea-formaldehyde resins and formaldehyde-tanned leather. It is, however, not impossible that compounds of the type assumed by such a theory (*e.g.* dimethylol urea) may be produced as the result of the prolonged ageing of leather which has been tanned in high concentrations of formaldehyde; however, the present data have no bearing on this point. J. G.

Inorganic

Tetraphenylarsonium Chloride as an Analytical Reagent. H. H. Willard and G. M. Smith. (*Ind. Eng. Chem., Anal. Ed.*, **1939**, **11**, 186–188.)—The tetraphenylarsonium ion is likely to have uses as a reagent owing to its ability to form (*a*) insoluble salts by combination with ions such as perrhenate, permanganate, periodate and perchlorate, (*b*) insoluble complex mercuric, stannic, cadmium and zinc compounds, and (*c*) insoluble complexes with thiocyanate compounds of cobalt and iron. Applications of the reagent are to be given in subsequent papers; the present one is confined to the determination of the tetraphenylarsonium ion by potentiometric titration with iodine. The reaction involves combination of the ion with iodine and iodide: $(C_6H_5)_4As^{\bullet}+I_2+I' \rightarrow (C_6H_5)_4AsI_3$, the product, a rusty-orange precipitate, being insoluble in saturated sodium chloride solution. The potentiometric standardisation of tetraphenylarsonium chloride reagent solution is carried out as follows: Five to 10 ml. of the 0·01 to 0·03 *M* reagent solution are diluted to about 100 ml.; the reference and indicator electrodes are immersed in the liquid, which is titrated slowly, with constant stirring, with 0·02 *N* iodine solution containing 6 to 8 g. of potassium iodide per litre. During the titration the potential of the system decreases to a minimum; at the end-point there is a sudden increase in potential amounting to 25 to 35 millivolts per 0·01 ml. of 0·02 *N* iodine solution. Near the end-point the solution must be completely saturated with sodium chloride before the titration is completed. A smooth platinum wire and a calomel half-cell were used as indicator- and reference-electrodes respectively. The solution must be neutral or slightly acid. The alkalis and alkaline earths, nickel, cobalt(ous), chromium, manganese, borate, bicarbonate, acetate, phosphate, sulphate, citrate and tartrate, even in fairly high concentration, do not interfere. Nitrate in limited amount is allowable in neutral solution. S. G. C.

Modification of Bettendorff's Arsenic Test. W. B. King and F. E. Brown. (*J. Amer. Chem. Soc.*, 1939, **61**, 968–969.)—It has already been shown (*Ind. Eng. Chem.*, *Anal. Ed.*, 1933, **5**, 168) that traces of mercuric chloride hasten the reduction of arsenic compounds by stannous chloride, and that the time required for the appearance and development of the arsenic suspension is a function of the concentration of mercuric chloride in the solution. The present work shows that the modified Bettendorff's test is catalytic and not induced. One hundred ml. of a mercurous chloride solution of 9×10^{-7} molar strength were saturated with chlorine gas and left overnight; the excess of chlorine was then swept out completely by a current of hydrogen chloride gas. Two hours were required for the greenish-yellow colour to disappear. Another sample of 100 ml. was saturated with hydrogen chloride gas; and the oxidised and non-oxidised solutions were compared as regards their catalytic effects by noting the length of time required for a changing suspension to become darker than an unchanging standard. Mercurous and mercuric chloride solutions were found to have equal catalytic powers, and it is concluded that the actual catalyst is the mercury atom formed by reduction of the salts. D. G. H.

Interaction of Zinc Salts with Alkalis. A. I. Nikurasin. (*J. Ob. Chemie.*, **1938, 8, 1463–1464.**)—The precipitation of zinc hydroxide with alkalis from solutions of the chloride and sulphate has been investigated potentiometrically, hydrogen, glass, zinc amalgam and mercuric oxide electrodes being used. For complex systems the *p*H is measured in separate samples, as the composition of the system changes during potentiometric titration; hence the conditions are near those of equilibrium and the investigation is made with a constant volume of solution. The titration curves show that a basic salt, having one molecule of zinc salt to 3 molecules of zinc hydroxide, is first formed; this reacts with more alkali to form zinc hydroxide. Hysteresis, which is shown by the difference in the direct and reverse titration curves, is due to the slowness of the second stage. With a mercuric oxide electrode, the titration curves indicate the presence of acid and neutral zincate in solution at room temperature; the existence of the latter is confirmed by the curve with the zinc electrode. The curve for the titration of conc. sodium hydroxide with zinc chloride supports the hypothesis that sodium zincate, Na_2ZnO_2, first reacts with zinc chloride to precipitate zinc hydroxide and then slowly with the precipitate to form the difficultly soluble acid zincate. E. B. D.

Reaction of Tantalum, Niobium (Columbium) and Vanadium with Iodine. F. Korősy. (*J. Amer. Chem. Soc.*, **1939**, **61**, **838–843**.)—Tantalum, niobium and vanadium react with iodine vapour at dull red heat. Tantalum pentaiodide is stable, at least up to 500° C., but niobium and vanadium pentaiodides easily dissociate at their sublimation temperatures (about 400° C.). Incandescent tantalum wire will reduce tantalum pentaiodide in the vapour phase. The lower tantalum iodides, intermediate between the pentaiodide and metallic tantalum, may be obtained in nearly any desired average composition, but only one deep green compound can be extracted therefrom with water. The green ion was found to be charged positively, and the product is regarded as probably an analogue of Chapin's green chloride and bromide (*J. Amer. Chem. Soc.*, 1910, **32**, 323). A lower iodide of niobium was found to be stable *in vacuo* up to 500–600° C., and is probably a definite compound. Niobium iodides, when heated, gave products with the formula Nb_6I_{14} (? Nb_2I_5), whilst the formula V_2I_3 was calculated for the dark reddish-brown vanadium iodide obtained when the pentaiodide sublimes. Details are given for the various reactions together with the physical properties of some of the compounds. D. G. H.

Reactions of Resorcinol with Niobium and Tantalum. F. M. Shemjakin and V. A. Pilipenko. (*J. Ob. Chimie*, 1938, 8, 824–828.)—It was stated by Platonov, Krivoshlikov and Marakaev (*J. Ob. Chimie*, 1936, 1815) that in ammoniacal solution resorcinol gives blue, bluish-green and greyish-green colours with niobium, tantalum and titanium respectively. As similar blue or green colours are also given by zinc, calcium and nickel, and as an ammoniacal or alkaline solution of resorcinol alone gradually gives a bluish-green colour which changes to yellowish-green, the reaction is obviously not specific for the above-mentioned metals. The authors have investigated the colour reactions of potassium niobium fluoride and potassium tantalum fluoride by the method of Gibbs's triangle. The tantalum compound was prepared by Treadwell and Hall's method, but with the use of Merck's perhydrol instead of nitric acid. The results for the 36 divisions of the triangles are illustrated for solutions of the fluorides in potassium hydroxide (results in ammoniacal solution in the presence of ammonium oxalate were negative). It was found that tantalum changed the colour of resorcinol from a greenish-yellow shade to yellow or yellowish-orange at a series of points; at a few points a flocculent yellow precipitate was formed. With niobium the same colour was usually obtained as with resorcinol alone, but in some regions the colour disappeared completely. These results also indicate that the reaction is not specific for niobium and tantalum. Similar colour reactions of cerium, other rare earths and their related elements have been studied. Most of these yield a blue or bluish-green precipitate in ammoniacal solution. In a solution of potassium hydroxide the precipitates formed are of various colours. E. B. D.

Determination of Strontium in the Presence of Calcium. R. N. Shreve, C. H. Watkins and J. C. Browning. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 215.)—The solution containing strontium and calcium as nitrates is acidified with nitric acid and evaporated to dryness on a steam-bath. The mass is cooled, and 25 ml. of anhydrous acetone are added and allowed to remain in contact with the solid for one hour with occasional shaking. Calcium nitrate dissolves, and the residue of strontium nitrate is filtered off on a Gooch crucible, washed with acetone, dried and weighed. Tests on mixtures of 1 to 2 g. of strontium nitrate with 0·1 to 2 g. of calcium nitrate, showed that the percentage recovery of strontium nitrate was 99·7 to 99·9. Strontium and calcium, present as chlorides, may be conveniently converted into nitrates by precipitating them as carbonates with ammonium carbonate and dissolving the washed precipitate in nitric acid. S. G. C.

Colorimetric Determination of Chlorine with *p*-Aminodimethylaniline. D. H. Byers and M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 202–203.) —A spectrophotometric study of this method for the determination of residual chlorine in water has been carried out. A purple colour is produced, and the sensitiveness is 0·01 to 0·03 p.p.m. It is stated that the method seems to have no advantage over the more familiar *o*-tolidine method unless there is an individual preference for matching purple rather than yellow hues. S. G. C.

Improved Molybdenum Blue Reagents for Determination of Phosphorus and Arsenic. J. A. Schricker and P. R. Dawson. (*J. Assoc. Off. Agric. Chem.*, 1939, **22**, 167–179.)—In Zinzadze's method for the quantitative determination of minute concentrations of phosphorus and arsenic (*Z. Pflanzenern. Düng. u. Bodenk.*, 1930, **16** (A), 129; **1932, 23,** 447; Abst., ANALYST, **1932, 57,** 411; *Bull. Soc. chim.*, **1931, 49,** 872; *Ind. Eng. Chem., Anal. Ed.*, **1935, 7,** 227, 230; *Z. Unters. Lebensm.*, **1935, 70,** 308; Abst., ANALYST, **1936, 61,** 198) the conditions for minimum interference by silica and salts have been studied. For phosphorus they are: molybdic oxide concentration, 0·0018 M; sulphuric acid concentration, 0·36 N; and reduction concentration, 0·0004 N; for arsenic the same sulphuric acid and reduction concentrations are required, but the molybdic oxide concentration should be 0·0032 M (the term "reduction concentration" applies to the concentration of quinquevalent molybdenum oxide resulting from reduction of the sexavalent molybdenum oxide). To attain these conditions the concentrated reagent for phosphorus has molybdic oxide, sulphuric acid, and reduction concentrations of 0·18 M, 36 N, and 0·040 N respectively, whilst the molybdic oxide concentration in the arsenic reagent has the value 0·32 M; the reagents are therefore conc. sulphuric acid solutions of 0·02 M $Mo_{10}O_{29}$ for phosphorus and 0·02 M $Mo_{17}O_{50}$ for arsenic. Zinzadze's reagent is further modified by the substitution of quinaldine red for β-dinitrophenol as an indicator for preliminary adjustment of the *p*H of the test solution, so that the final *p*H remains well below 1·0 when the molybdenum blue reagent is added, and by the use of sulphurous acid instead of sodium bisulphite. The following methods are recommended.

METHOD A, PHOSPHORUS.—(*a*) *Molybdenum blue for phosphorus.*—Pure molybdenum trioxide is ignited in a porcelain dish at a dull red heat and below its m.p. in a muffle furnace for about 1 hour and then cooled. A quantity of 6·96 g. is boiled gently in a 500-ml. Kjeldahl flask with 250 ml. of conc. (36 *N*) sulphuric acid and a few glass beads until solution is complete (a slight cloudiness does not matter). The liquid is cooled to about 150° C. and 0·16 g. of pure powdered molybdenum metal is introduced carefully down the neck of the flask. The flask is rotated occasionally for 10 minutes, after which the metal should be completely dissolved; if there is any residue the liquid is heated again to 150° C. When solution is complete the liquid is cooled, and a convenient portion (5 or 10 ml.) is diluted with about 5 volumes of water and titrated with 0·1 *N* or 0·02 *N* potassium permanganate solution, the end-point being the appearance of a pink colour lasting for 1 minute. The reduction concentration of the solution, which should be about 0·04 *N*, is calculated from the result. If the reduction concentration is less than 0·036 *N*, a calculated quantity of molybdenum sufficient to bring the concentration up to about 0·04 *N* is added and the liquid is re-heated to 150° C. and then cooled, and the titre is checked again. The bright blue solution is kept in a glass-stoppered bottle. (*b*) *Standard phosphate.*—Aqueous monopotassium phosphate solutions containing 1, 10, 100, etc., γ of phosphorus per ml. are prepared. (*c*) *Determination of phosphorus.*—To an aliquot part of the phosphorus solution in a 50-ml. volumetric flask there is added 1 drop of 0·01 per cent. aqueous quinaldine red solution, followed by dilute solutions of sodium carbonate or sulphuric acid until the red colour just disappears. Water is added to about 25 ml. and then 5 ml. of a saturated solution of sulphur dioxide or of a solution obtained by dissolving 5·2 g. of pure sodium bisulphite in 100 ml. of *N* sulphuric acid (this solution must be prepared weekly and kept stoppered). The liquid is digested on the steam-bath for 30 minutes or for 20 minutes after the temperature has reached 95° C.; if the sample is comparatively free from arsenic and nitrate (not more than 50γ) this time may be shortened to 10 minutes. Half a ml. of the molybdenum blue reagent is run down the neck of the flask, to avoid spurting. The neck of the flask is rinsed down with two or three drops of water, the liquid is mixed, and digestion is continued for 30 minutes. The liquid is cooled, made up to 50 ml. and mixed, and the colour is read against a standard similarly prepared or, preferably, in a photoelectric colorimeter. It is desirable to read the colours within 4 hours, as there is a 2 to 5 per cent. fading during the first 24 hours, but this difference is detectable only by a photometer, so that the fading does not preclude the reading, by ordinary colorimetric methods, of colours left overnight. After 24 hours, if the flasks are stoppered, the colours remain quite stable for a week or more, even when exposed to light.

METHOD B, PHOSPHORUS.—(*a*) *Sulphomolybdic acid.*—A quantity of 7·2 g. of ignited pure molybdic oxide is dissolved in 250 ml. of conc. sulphuric acid as in method A. The reagent is cooled and stored in a glass-stoppered bottle. (*b*) *Determination of phosphorus.*—The method is the same as method A up to the end of the digestion with sulphurous acid or sodium bisulphite. Half a ml. of the sulphomolybdic acid reagent and 1·0 ml. of metol solution (0·42 g. of methylparamidophenol sulphate and 6·3 g. of sodium sulphite in 100 ml.) are pipetted in with the same precautions as in A. The digestion is continued for 30 minutes on the steam-bath, and the liquid is cooled, made up to volume, mixed, and read as in A. In the absence of appreciable quantities of arsenic and nitrate the preliminary digestion may be shortened as in A. These reagents are affected by iron, arsenic and nitrate when the quantities of these are greater than 10 mg., 1 mg., and 1 mg., respectively. The sensitivities of the two methods for phosphorus are practically identical, but method B shows a somewhat more rapid development of colour.

METHOD C, ARSENIC.—(*a*) *Molybdenum blue for arsenic.*—The procedure is the same as for preparing the molybdenum blue reagent for phosphorus under A, but 12 g. of molybdic oxide is used per 250 ml. of sulphuric acid. (*b*) *Standard arsenate.*—Aqueous monopotassium arsenate solutions containing 1, 10, 100, etc., γ of arsenic per ml. are prepared. (*c*) *Determination of arsenic.*—The aliquot part must be free from nitrate, phosphorus and arsenic in the quinquevalent form (a previous separation by trichloride distillation into water followed by evaporation of the distillate with an excess of nitric acid to the complete elimination of hydrochloric acid and nitric acid is probably the most satisfactory: Deemer and Schricker, *J. Assoc. Off. Agric. Chem.*, 1933, **16**, 226). The residue is dissolved and washed with hot water into a 50-ml. flask, and the liquid is neutralised to quinaldine red, as directed under A and B, and made up to about 30 ml. Half a ml. of the molybdenum reagent is added, and the liquid is digested on the steam-bath for 30 minutes, cooled, made to volume, mixed and read as directed under A (see also Abstract, p. 432–434). E. M. P.

Microchemical

Applications of Spot Tests to Analysis of Medicinal Preparations. VI, VII, VIII, and IX. O. Frehden and K. Fürst. (*Mikrochem.*, 1938, **25**, 256–258; 1939, **26**, 36–38, 38–40, 40–43.)—VI. *Test for formic acid.*—The test, which depends on the detection of carbon dioxide liberated by the action of bromine ($HCOOH + Br_2 \rightarrow 2HBr + CO_2$), is made in Feigl's apparatus (F. Feigl, *Spot Tests*, English trans., 1937, p. 11, Fig. 16) for micro-distillation and collection of evolved gases. A few drops of the test solution are placed in the bulb of the apparatus and treated with bromine water, drop by drop, until the yellow colour persists. A few splinters of quartz are added to prevent spurting, a drop of a saturated solution of barium hydroxide is placed in the glass tube which serves as a stopper for the apparatus, and the bulb is heated over a micro-burner until its contents boil. The baryta turns cloudy when formic acid is present. For small amounts a blank test is advisable. The barium hydroxide is covered with a thin layer of liquid paraffin to prevent it coming into contact with the air. As little as 2·5γ of formic acid may be detected.

VII. *Test for polyhydroxy compounds.*—The formic acid test (see above) may be applied after oxidation of the polyvalent alcohols with periodate in sulphuric acid solution to formaldehyde and formic acid. A little of the sample is placed in Feigl's apparatus (see above) together with 2 drops of a saturated solution of sodium periodate and 2 drops of N sulphuric acid, and warmed gently. The procedure described above, for formic acid, is then followed. The following substances were tested, the amounts in brackets being the smallest quantity to give a positive reaction in each instance:—glycerol (2·5γ), mannitol (3γ), dextrose (5γ), laevulose (5γ), arabinose (5γ), mannose (2·5γ), maltose (2·5γ), sucrose (7γ), lactose (6γ), dextrin (6γ), starch (20γ), and mucic acid (3γ). The test may be carried out in the presence of aldehydes, with the exception of formaldehyde.

VIII. *Test for aldehydes.*—The test depends on the fact that malachite green which has been decolorised with sodium sulphite regains its colour on the addition of aldehydes. The test may with advantage be carried out on a stable reagent paper, prepared as follows:—0·8 g. of malachite green is dissolved as the leuco-base by heating it in presence of 3 g. of sodium sulphite; a further 2 g. of sodium sulphite are then added and the mixture is filtered. On cooling, crystals of the leuco-base are precipitated from the filtrate, which is then only pale yellow. Strips of thin filter-paper are immersed in the yellow solution and dried in the air. The impregnated paper should be quite white without even a trace of green; when stored in a stoppered bottle it will keep for several weeks. When a drop of the neutral test solution is added to the reagent paper a green colour indicates aldehydes. The solution must be neutral, since both acids and alkalis change its colour. In a series of tests with 20 aldehydes amounts varying from 20 to 300γ were detected.

IX. *Test for free chlorine and substances containing chlorine.*—This test, due to Frehden and Chen-Hua Huang, depends on the interaction of chlorine with potassium bromide to liberate bromine, which is recognised by its action in converting fluorescein into eosin. Stable spot-paper for the reaction is prepared by immersing it in a solution of 0·1 g. of fluorescein in 100 ml. of dilute alkali containing 0·5 to 0·8 g. potassium bromide, and drying it in the air. When the vapour or solution to be tested is brought into contact with the pale yellow reagent paper a violet-red spot is formed if free chlorine is present. The test is not applicable in the presence of other free halogens, but other oxidising agents in general give no reaction, and the test is therefore preferable to one involving the use of starch-iodide paper. Chlorides can be detected after liberation of their chlorine by heating with sulphuric acid and manganese dioxide. The test can be used for the detection of free chlorine in washing soaps, bleaching agents, medicinal chloroform, drinking water, dyes, gases, etc. J. W. M.

Micro-test for Palladium. R. Schoental. (*Mikrochem.*, 1938, **24**, 20–21.)—Solutions of *p*-amino-acetophenone form a yellow complex salt with palladium salts in neutral or slightly acid solutions. The complex salt is insoluble in cold water, dilute acids, alcohol, ether, acetone or chloroform. Strong alkalis decompose both the reagent and the complex salt. The reaction is extremely selective and may be used for the separation of palladium from other cations, especially in the platinum group (Pt, Ir, Os, Ru, Rh), and also from gold and tellurium. Only cerium salts interfere and must be removed before carrying out the test. The reagent is used in a 1 per cent. aqueous solution containing 2 ml. of conc. hydrochloric acid. When the test solution is mixed with an equal volume of the reagent a cloudiness is perceptible with as little as 5γ of palladous chloride per ml. When the test is made on a microscope slide and the precipitate is examined under the microscope 0·75γ of palladous chloride can be detected. The reaction may also be adapted to quantitative nephelometric analysis. J. W. M.

Micro-determination of Manganese in Biological Materials. A. C. Wiese and B. C. Johnson. (*J. Biol. Chem.*, **1939**, **127**, 203–209.)—A method capable of determining 0·1 to 10γ of manganese has been based on oxidation of the manganese to permanganate with sodium bismuthate and addition of the permanganate solution to a strongly acid solution of benzidine in nitric acid. This causes the formation of a yellowish-green colour instead of the blue colour obtained in dilute acetic acid solution; the former colour is much more stable. A sample containing 1 to 10γ of manganese is weighed and ashed in a well-extracted porcelain dish at cherry-red heat. The ash is digested with a boiling mixture of 3 to 5 ml. of conc. nitric acid and 10 ml. of water, and the solution is transferred to a beaker and evaporated to dryness. The residue is digested with 3 to 5 ml. of conc. nitric acid and 10 ml. of water and the solution is evaporated. This process is repeated a third time to ensure complete removal of chlorides, which cannot be removed by precipitation with silver nitrate solution, as excess of this interferes in the later stages of the determination. The final residue is dissolved in 3 ml. of conc. nitric acid and 10 ml. of water, and the solution is boiled for 2 to 3 minutes with 0·2 g. of sodium bismuthate to remove oxides of nitrogen. After being cooled to below 30° C. the solution is mixed with 0·3 to 0·5 g. of sodium bismuthate and left for a few minutes. The excess of sodium bismuthate is filtered off in a Gooch crucible, and the filtrate is collected in a colorimeter tube containing 3 ml. of redistilled water and 2 drops of a 1 per cent. solution of benzidine in 5 per cent. acetic acid. (The benzidine used was specially purified by crystallisation from 70 per cent. alcohol, decolorisation with charcoal and recrystallisation, followed by a second recrystallisation from benzene.) The solution is made up to 25 ml. and thoroughly mixed. The yellowish-green colour that develops is measured after 5 minutes in an Evelyn photo-electric colorimeter with a 420mμ filter. The instrument is calibrated by means of solutions containing known amounts of manganese and treated in the same manner. A Dubosq colorimeter can be used instead of the photo-electric colorimeter, but the procedure is not so sensitive or so rapid. Amounts of manganese between 0·1 and 1·0γ were determined with an error of 20 to 30 per cent., but with amounts between 2 and 15γ, the error was generally only about 2 per cent. When manganese was added to various materials recoveries ranging from 92 to 106 per cent. were obtained. F. A. R.

Physical Methods, Apparatus, etc.

Determination of Water in Acetone by means of the Infra-red Absorption-Spectrum. R. Gaspart and L. Gillo. (*Bull. Soc. Chim. Belge*, **1939**, **47**, 933–939.)—The infra-red absorption-spectrum of mixtures of acetone and small amounts of water has a characteristic double band consisting of an intense band of wave-number 3550 cm.$^{-1}$ corresponding with a state of molecular association between water and acetone, and a less intense band of wave-number **3580 cm.$^{-1}$*** Methods based on the measurement of these bands have already been described and applied to the determination of 250 parts per 100,000 of water in acetone (*cf.* Errera and others, *Physica*, 1937, **4**, 1097; 1938, **5**, 116; *cf.* also *Trans. Faraday Soc.*, 1938, **34**, 729), and the present authors have now extended them to acetone containing even smaller concentrations of water. The acetone was distilled in a Swietoslawski ebullioscope provided with 2 Beckmann thermometers showing the temperature of the boiling liquid and of the condensing vapour. By means of a calibration-curve it was possible to determine the concentration of any mixture from the difference between the two temperatures. The outlet of the apparatus was connected directly with the observation cell, the exit of which was connected through a condenser with a receiver, all outlets to the air being protected by tubes containing phosphorus pentoxide. At the beginning of the distillation the cell was "rinsed," and all traces of moisture were removed from the air within it by maintaining it at a temperature slightly above the b.p. of acetone; the inlet and outlet tubes of the cell were finally sealed in a flame. It was thus possible to fill the cell with pure acetone or, by the use of constant-boiling mixtures, with acetone containing known quantities of water. Curves are shown relating the wave-number of the light used (3800 to 3400 cm.$^{-1}$) with the percentage of light transmitted by a layer of 1 ml. of the sample (1 mm. thick), as compared with carbon tetrachloride; corrections were applied for reflection effects produced at the parallel faces of the cells. A comparison of the curves for pure acetone and for acetone containing 1, 2·5 and 5 parts of water per 100,000 shows that quantities of water of the order of 1 part per 100,000 may be detected from the marked depression in the transmission ratio at a wave-number of 3618 cm.$^{-1}$, corresponding with the more intense of the bands due to water. It is then shown how the actual concentrations of water may be determined from the formulae, $T = e^{-kd}$ and $T = e^{-xcd}$, where T is the measured transmission, k the coefficient of extinction, x the molecular coefficient of extinction, c the concentration of water (in g.-mol. per litre), and d the thickness of the cell in cm. The concentrations of water found for the three solutions were, respectively, 1, 4 and 9·5 (± 1) parts per 100,000 for the ebulliometric method; 0·7, 2·2 and 5 parts per 100,000 for the spectroscopic method, the possible errors for the latter being 100, 25 and 10 per cent., respectively. The values of x obtained for the three solutions (2090, 1850 and 1260, respectively) decrease as the concentration increases, so that the Beer-Lambert law is not followed completely, and therefore for exact quantitative work it is necessary to work from a calibration curve based on experimental values obtained with solutions of known concentrations and showing the relationship between k and c. J. G.

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* The frequency, *i.e.* the number of vibrations per second, is found by dividing the velocity of light by the wave-length λ, but spectroscopists have found it more convenient to use the simple reciprocal of the wave-length, *i.e.* $1/\lambda$ instead of C/λ, λ being expressed in cm. This reciprocal gives the number of waves per cm. length and is known as the wave-number. For example, a wave-number of 3618 cm.$^{-1}$ corresponds with a wave-length of $\frac{1}{3618}$ cm. = $2{\cdot}764 \times 10^{-4}$ cm. = $2{\cdot}764\mu$.—EDITOR.

Errata—*February Issue*

P. 133, l. 6 from bottom, *for* "2 litres of water are added" *read* "made up to 2 litres."
P. 134, l. 1, *for* "in strong daylight" *read* "strong daylight being avoided."
P. 135, l. 6, *for* "$0{\cdot}2G^2$" *read* "$0{\cdot}02G^2$."
P. 134, l. 18, the prescription of 50 ml. is unnecessary.

Reviews

SPECTROCHEMICAL ANALYSIS IN 1938. A companion book to "Spectrochemical Abstracts 1933–38." By F. TWYMAN, F.R.S. Pp. 68. London: Adam Hilger, Ltd. Price 4s. 4d.

As the title indicates, this monograph adds to the information given in the earlier publications. It incorporates two reports published in the Annual Report of the Chemical Society for 1937 and in the *Journal of the Society of Chemical Industry*, 1938. Both were well worth reprinting, the first because it deals generally with various methods of exciting spectrum lines and with their measurement; the second with the theory and practice of microphotometry as applied to the quantitative determination of the constituents of alloys when present in small amounts. The latter report treats in detail of precautions necessary for the examination of alloys and is illustrated by reference to the quantitative analysis of aluminium alloys. A short chapter is devoted to discrepancies between chemical and spectrochemical analysis, and reasons are advanced for attributing the discrepancies to the heterogeneity of the alloy. If this be accepted, it follows that in important cases chemical analysis should be employed to obtain a measure of the overall proportion of a constituent or impurity, and spectrochemical analysis to ascertain the variation in this constituent. When the proportion of the constituent is small in amount, say less than 0·3 per cent. or thereabouts, the spectrochemical method is accurate enough to show when heterogeneity is present. A few pages are devoted to sparking circuits, and a very good case is made out for considering that the methods developed by Twyman and his co-workers are as accurate and convenient as any of the more elaborate methods proposed abroad.

Mr. A. C. Candler summarises usefully the elements of the theory of atomic spectra. The reviewer's only comment on this summary is that it is so condensed that the beginner will have to consult more complete accounts if he desires to understand the subject fully. One such account is furnished in Candler's two volumes on "Atomic Spectra," where the subject is dealt with in much more detail.

An important aim of the monograph is to give the best technique for routine analysis of metals or alloys. Taken in conjunction with earlier monographs issued by the present publishers, this claim can be accepted as established.

It is gratifying to note that in the last few years an impressive number of British firms, individuals and institutions have turned to spectrochemical methods of analysis, and it is fortunate that the wide experience of the staff of Messrs. Hilger is available in this field.

J. J. FOX

HANDBOOK OF CHEMICAL MICROSCOPY. Vol. I. By E. M. CHAMOT, B.S., Ph.D., and C. W. MASON, A.B., Ph.D. Second Edition. Pp. xvi + 478, with 165 figures. London: Chapman & Hall, Ltd. 1938. Price 22s. 6d. net.

There is perhaps no other physical instrument adaptable to such a wide range of uses as the microscope, and the contents of this volume serve as a detailed guide to its manifold applications.

At the present time the terms micro-chemistry and chemical microscopy are not infrequently confused, but whilst the former should be applied to the detection and estimation of extremely small amounts of substances for which magnification is rarely necessary, the latter refers to the use of the microscope in the observation of the results of chemical reactions, and in qualitative and quantitative physical and physico-chemical determinations on a wide range of pure and industrial materials. These procedures have many advantages over the usual methods of examination, notably in the small size of the sample required, the avoidance in many instances of the destruction and loss of the material and the great saving of time ensured by eliminating tedious chemical analyses.

The arrangement of the subject-matter in the present volume is identical with that of the previous edition reviewed in THE ANALYST (1930, **55**, 470) and has copious foot-note references throughout the text.

The field of chemical microscopy is rapidly extending and this has necessitated the insertion of much new matter of considerable value. This includes the application of the Christiansen effect to colour filters in which the transmitted light is dependent upon temperature, "polaroid" filters, the centrifuge microscope, the "electron microscope" in which extremely high magnifications are obtained by the use of rays having a wave-length of 0·05 A.U. the Jelley grating microspectrograph, and the newer types of low-voltage incandescent electric lamps. For the benefit of the student descriptions are given of over one hundred experiments relating to the use of polarising apparatus, determination of the optical characteristics of various isotropic and anisotropic substances, the preparation of crystals and the determination of the refractive indices of solids and liquids. These in conjunction with the synopsis, in the appendix, of the laboratory practice adopted at Cornell University, form an excellent basis for training in the application of microscopic methods. So much of the chemist's ordinary physical work is now becoming mechanised that there is a great tendency towards a development of mental stasis in its application, but in the practice of chemical microscopy the mind of the observer must be continually on the alert to interpret correctly the phenomena observed.

The authors have covered a very wide field in their book, although Barger's molecular weight method and the vapour density method of Blackman appear to have been omitted, but these may perhaps be given in Vol. II, to be published later. Very brief references only are made to mineralogy, metallography and the biological sciences, since these are adequately dealt with in other works, but the general methods described in this volume are in many instances applicable to these branches of science.

The text is thoroughly up to date, including references to apparatus and methods described up to July, 1938, and it has been produced with the care and precision displayed in the earlier edition. A few very minor typographical errors are evident, and the transatlantic source of the volume is indicated by the presence of such verbs as "diaphragmed" (p. 45), "paralleling" (p. 77) and "diagrammed" (p. 126)—words that would make the flesh of our etymologists creep. A high degree of accuracy is evident in the text, references and index, but it may be suggested that the index would be of greater value had more cross-indexing been introduced.

This production maintains the lucidity and reliability of its predecessors, and may be thoroughly recommended, not only to the student, but to all engaged in the practice of pure or applied chemistry, for in addition to its instructional value it forms a comprehensive guide to most of the international literature of the subject.

T. J. WARD

RECENT ADVANCES IN CHEMOTHERAPY. By G. M. FINDLAY, C.B.E., M.D., D.Sc. 2nd Edition. Pp. x + 523. London: J. & A. Churchill, Ltd. 1938. Price 21s.

As a result of the recent discovery of the sulphonamide drugs, interest in chemotherapy has been greatly stimulated and the search for new chemotherapeutic substances is being more actively pursued throughout the world. The timely appearance of the second edition of this book will therefore be much appreciated, presenting as it does an up-to-date survey of the knowledge and progress in this field. Indeed, the title scarcely does justice to the wide scope of the treatment, for the earlier work is as carefully summarised as the more recent discoveries.

In the course of revision the book has been practically re-written in order to make room for accounts of important advances and to augment the earlier work with further clinical results. Nevertheless, the essentials of the original form are retained, a chapter being allocated to each infection or group of infections, ranging from those due to helminths to diseases resulting from ultra-microscopic viruses.

Many new chemotherapeutic substances are described and, where available, full information is given regarding their clinical effectiveness, toxicity, pharmacology and use in treatment and prophylaxis.

Among the anti-malarials Plasmoquin and Atebrin represent a considerable advance, although quinine still ranks first on account of its effectiveness, low toxicity and the widespread familiarity with its use. The search for more active and less toxic substances is still proceeding, and the results of investigations of numerous homologues of Plasmoquin are given.

In the chapter on trypanosomiasis new organic arsenicals are described, notably the aryl thioarsinites. In addition, there are the interesting polymethylene amidines and guanidines whose constitution is entirely different from that of any other known trypanocides. Undecamethylene diamidine, the most active and least toxic member of the series, is also reported as having a temporary action on certain types of malaria.

The most outstanding developments recorded are, of course, in connection with the sulphonamide drugs. The discovery of these substances is described by the author in his preface as equal to, if not greater than, the introduction of

Arsphenamine by Ehrlich. This is surely no exaggeration, as an examination of the long chapter on acute bacterial infections will prove. Although it is not possible here to give more than the briefest summary of this section, it may be said that it represents a condensed account of all important developments in the subject, from the discovery of Prontosil to the appearance of M. and B. 693, which is proving so useful in the treatment of pneumococcal infections.

Mention must also be made of the diphenyl sulphones which have been shown to possess, for certain experimental diseases, a therapeutic effect comparable with that of sulphanilamide.

Another advance, which has been rather overshadowed by the success of the sulphonamide drugs, is the use of mandelic acid in the treatment of bacillary infections of the urinary tract. Although, in some instances, it has been shown to be inferior to sulphanilamide, mandelic acid is far less toxic and is highly effective in certain streptococcal infections for which sulphanilamide is practically useless.

The chapter on virus infections is interesting because there are indications that a successful chemotherapy is becoming possible. The stimulus is again provided by sulphanilamide which has been shown to be effective in the case of at least one disease of this origin.

The only chapter that has been omitted from this edition is the short one on cancer, and in view of all the successes in the other fields one's hopes are raised that even this disease will eventually yield to chemotherapy.

Whilst this book may be of greatest value to the experimental pathologist and clinician, yet there is much to interest the organic chemist who may be called upon to produce new substances for chemotherapeutic investigation. Although no general relation between structure and therapeutic effect is discernible, variations in the molecule of certain drugs are seen to follow rough rules as regards the effect upon activity and toxicity. These generalisations are recorded and will be of considerable value in connection with the synthesis of derivatives and homologues of known active substances.

In conclusion, attention must be drawn to the excellent bibliography appearing at the end of each section, to which reference is made in the text.

G. E. H. SKRIMSHIRE

FUNDAMENTAL PRINCIPLES OF BACTERIOLOGY, WITH LABORATORY EXERCISES. By A. J. SALLE, B.S., M.S., Ph.D. First Edition. Pp. 679. London: McGraw-Hill Publishing Company, Ltd. 1939. Price 24s. net.

This book deals with fundamental principles and facts concerning the science of bacteriology. It is primarily intended for beginners, and the author has endeavoured to give explanations of all phenomena described, but it is not merely elementary; it is intended to provide the student with a solid foundation upon which to build for more specialised work and will be found to contain a great deal of detail. Thus in the chapter on Nutrition we find a good account of the requirements of different groups of bacteria:—the groups that require typtophane and the groups that do not; the groups that require vitamins and the groups that can synthesise their own; of the V and X factors required by ***Haemophilus influenzae***. The essential organic and inorganic chemistry involved in staining, disinfection, enzymes, respiration, industrial fermentations, nutrition and so forth are included. The biological stains are classified, graphic formulae are given and chromophores are indicated. Thus the book is written as a combined text-book and laboratory manual, the experimental portion being woven into the body of the text under the appropriate chapters.

The headings of the chapters, which are as follows, convey a fair idea of the scope of the work:—Introduction, General Laboratory Instructions, The Nutrition of Bacteria, The Microscope, Biological Stains, The Morphology of Bacteria, The Yeasts, The Moulds, Pure Culture Technique, Influence of Environment upon Bacteria, Disinfection and Disinfectants, Enzymes of Bacteria, The Respiration of Bacteria, Protein Decomposition, Industrial Fermentation, The Differentiation and Classification of Bacteria, The Bacteriology of Water, The Bacteriology of Soil, The Bacteriology of Air, The Bacteriology of Milk and Milk Products, The Bacteriology of Foods, Bacterial Diseases of Plants, Bacterial Dissociation, Infection and Immunity, Specific Infections, History of Bacteriology, Preparation of Solutions and Stains, and Preparation of Culture Media. These subjects are fully dealt with and anyone who carefully studies the book and carries out a wise selection of the laboratory procedures described (of which there are no less than 111) will most certainly acquire a very ample and sound foundation from which to specialise in any of the branches of bacteriology.

The book is well written and arranged, and has a good index; it is well printed on excellent paper and attractively bound. From every point of view it is to be strongly recommended. D. R. WOOD

UNTERSUCHUNGSMETHODEN FÜR ARZNEISPEZIALITÄTEN. Fédération Internationale Pharmaceutique. Leyden. Second Edition. Pp. 148. Amsterdam: Dekker & Nordemann. 1938. Price Fl. 3·50.

There is no doubt that medicaments are ideal substances for administration in tablet form, and the public has no reason to complain that manufacturers fail to cater for its wants. Some will maintain that the glut of such articles has the disadvantage of encouraging self-medication; but it is certain that the convenient form of these preparations ensures their retention on the market, and an increase in number is to be expected in the future. The examination of such products is essential both for manufacturing control and for the protection of the purchaser; if well-tried methods can be standardised, advantage accrues to both maker and user. Such methods are usually available for pharmacopoeial or other official preparations; but the vast majority of tablets and pastilles are unofficial, and analysts are grateful when methods of standing are available for their examination.

The present volume is the second edition of methods of analysis for unofficial preparations drawn together by a Commission appointed by the Fédération Internationale Pharmaceutique. The Commission comprises representatives from Holland, Denmark, France, Sweden, Austria, Switzerland and Germany. The contents of the book are divided as follows:—10 pages to general physical methods, 7 to general chemical methods, 2 to the wet oxidation process for decomposition, 44 to quantitative determination of elements and certain compounds, 56 to the examination of tablets and pastilles (including a table of 88 substances with notes on their quantitative analysis), 3 to the determination of rarer metals, 8 to indicators and reagents, 8 to three tables, and 10 to preface, contents and index.

The methods appear to be wisely chosen, and sufficient practical details for standard technique are given. Inconsistency is shown in the references to original work. While some methods are correctly ascribed, some have no reference and others are attributed to authors who can by no means be regarded as originators. For example, the general method for determining alkaloids—extraction with chloroform from alkaline solution, evaporation and titration—is ascribed to papers in 1931 and 1932. Of the three tables given at the end of the book, two are acknowledged as taken from the United States and the Dutch Pharmacopoeias respectively, whilst there is no mention, other than in the Index, that the third is copied from the British Pharmacopoeia.

While dealing almost exclusively with analytical methods, standards are laid down for firmness, disintegrability and weight of tablets, and the quantity of active substance which should be present. The requirement for firmness is that tablets and pastilles, while kept in original containers, must not crack, nor the corners be appreciably broken. Three standards of disintegrability apply to tablets (except those which are required to dissolve slowly in the mouth), *viz.*,

(1) Tablets without coating must, after 10 minutes in water at body temperature, be dissolved, disintegrated or so far softened that they crumble with the slightest pressure.

(2) Coated tablets placed in water at body temperature must be so softened within 2 hours that both coating and content crumble with the slightest pressure.

(3) Tablets for absorption in the intestines must not be disintegrated within 2 hours at body temperature in water or in 0·1 *N* acid. In alkaline medium they must be sufficiently softened in 1 hour to crumble with the slightest pressure.

The standard for weight to ensure uniformity is as follows:

Weight of individual tablets	Greatest variation in 90 per cent. of the tablets
Below 0·25 g.	12 per cent.
0·25 to 0·50 g.	10 ,, ,,
Over 0·50 g.	6 ,, ,,

The remaining 10 per cent. of the tablets must not vary by more than double these amounts. The quantity of active substance present must not vary by more than 10 per cent. from the declared quantity (tablets within the above limits of weight being used).

These requirements and standards appear reasonable and should meet the practical considerations of manufacturers as well as the needs of the purchaser.

A few errors have been noted, but the only one of possible significance is in Table II where, owing to the figures spreading over several pages, the line which should be *over* certain digits on the top of the page, appears *under* digits at the bottom of the previous page.

The book is well printed and has an excellent index. It should prove of great value to those whose work requires the analysis of certain unofficial but not uncommon tablets.

J. R. NICHOLLS

ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND QUANTITATIVE. By C. G. LYONS and F. N. APPLEYARD. 13th Edition. Pp. 282. London: J. & A. Churchill, Ltd. 1938. Price 7s. 6d. net.

A book designed to fill the needs of a student working for a special examination can only be judged within the limits of that object. This one, based on the text of Clowes and Coleman, is intended to supply the descriptive chemistry and practical instruction required up to and including a pass degree in science, the preliminary scientific examination of the Pharmaceutical Society and the preliminary medical and dental examinations; in this object it should succeed admirably and concisely. It goes straight to the task of supplying, within the syllabus of the several examinations for which it is intended, the descriptive chemistry required, and stops at that; no space is devoted to the standing orders of any particular laboratory, to teaching the teacher, or to doing his work for him by lists of test questions.

If the original version and repeated revisions and editions are included, the book is now in its 27th thousand, but as it has been re-set, and the originators' names removed from the title page, it is obviously intended to be regarded as a new book, and as such may be appraised afresh.

As will be seen from some of the remarks above, it falls into the class of text-book that is more suited to those who "take chemistry" as part of the course for other professions than to those for whom it is the serious business of life; its chemistry is of that idealised type in which all ions are invariably present in sufficient quantity to be readily detected, and the limitations imposed by solubility product and co-precipitation are non-existent. It contains, however, a short section of nine pages on physico-chemical theory, with an indication where more may be found; just sufficient to remove from a student's mind any mistaken impression that chemistry is exclusively a descriptive science.

The somewhat old-fashioned appearance of the previous edition has been removed by a new set of illustrations; these are drawn in a surrealist style that shows no line to mark the rim of glass vessels, so that a beaker looks like a flat-bottomed letter "U," and a funnel like a hollow-stemmed "Y." Such unconventional diagrams will be considered by many a poor exchange for the artistic drawings of former editions. Take, for example, that of the stiff-cuffed wrists of the immaculate but invisible chemist of a bygone age, who has demonstrated so successfully and to so many students the proper method of pouring liquid from one vessel to another.

The task of bringing a time-honoured text-book into line with modern ideas, while keeping within the limits of a prescribed curriculum, is one not lightly to be undertaken. The present authors are to be congratulated on their production, which may be expected to meet for many years to come the needs of those for whom it is intended.

Reviews of the 11th and 12th editions appeared in THE ANALYST, 1931, **56**, 137, and 1935, **60**, 277.

F. L. OKELL

THE PLANT ALKALOIDS. By T. A. HENRY, D.Sc. 3rd Ed. Pp. viii + 689.
London: J. & A. Churchill, Ltd. 1939. Price 42s.

The prophecy that alkaloidal chemistry will still be the playground of the organic chemist a century hence, is probably a safe one. At the present rate of development this can be said of few other branches of organic chemistry. There are various factors which contribute to this situation, the most important of which is the lack of a system of mobilising the supply of raw plant materials from all quarters of the globe. The Amazonian forest, for instance, is full of alkaloid-bearing plants and trees, but nothing less than a costly expedition, equipped with expert botanists, can at present make any of these available in an authoritative form to science. The low yield of some alkaloids is another limiting factor, contents of 0·01 per cent. being not uncommon. This may be met in some cases by cultivation, for the colouring matters and alkaloids of many annuals and biennials have been made available to the chemist by growing the appropriate plant on a large scale on farms. The cultivation of tropical climbers, however, presents a much more formidable problem.

A further justification for the introductory statement may be seen in the fact that of 137 different alkaloids taken at random, probably about 10 per cent. are alkaloids of known constitution. In the book under review there are, for example, 31 alkaloids containing 15 carbon atoms, 33 containing 16 carbon atoms, 26 containing 17 carbon atoms and 47 containing 17 carbon atoms. As the number of carbon atoms in an alkaloid increases, so does, as a rule, the difficulty of solving the problem of its chemical constitution. Greater progress could be made in many cases with a more ample supply of material, but a few alkaloids with constitutions as difficult to disentangle as that of brucine or strychnine, whose structures are on the verge of solution after 40 years of intensive effort, may considerably retard the march of progress by their complexity.

This, the third edition of Henry's *Plant Alkaloids*, is the golden key opening the gate to this entrancing field, and, indeed, a source of inspiration for new advances in medicinal chemistry. With the progress in physiology and pharmacology, alkaloids which have hitherto been laboratory curiosities are daily entering into the service of medicine, and will no doubt continue to do so. The book has been entirely re-written, and the author's decision to omit discussion of the purine bases seems to be fully justified. In view of the expansion of the subject, it is hardly likely that a better book covering the whole alkaloidal field will ever be written by one individual. In the present production the balance between historical matter, experimentally ascertained chemical facts and pharmacology is well nigh perfect. The reader needs no reminder that several of the chapters owe their authoritative character to the experimental work of the author and his colleagues. The book is not unduly expensive, and the reproductions of the formulae are excellent. The volume is destined to remain the standard of reference for many years to come, not only to the university professor in search of problems for his students, but to the fine chemical manufacturer and all those whose activities impinge on the rapidly extending field of medicinal chemistry.

HAROLD KING

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Death

With deep regret we record the death of William Thomas Burgess, Vice-President in 1918–19.

The Evaluation of Hydrogen Peroxide

By S. M. TRITTON, M.P.S., F.I.C.

(*Read at the Meeting, April* 5, 1939)

Part I

Reagents for Evaluating Hydrogen Peroxide.—Hydrogen peroxide, as supplied for surgical and pharmaceutical purposes, has frequently been found to vary in its efficacy. This has not been found to be due to loss of strength of the peroxide, and it is therefore very likely either that the peroxide has been over-stabilised or that unsuitable stabilisers have been used. It seemed desirable to investigate this point.

The B.P.C. states that "Hydrogen peroxide owes its efficacy as an antiseptic to the readiness with which it liberates oxygen in the presence of living or dead tissues and bacteria," but there appears to exist no method for testing this ease of decomposition Since catalase is a factor in organic matter that catalyses the decomposition of hydrogen peroxide, with liberation of one atom of oxygen, it was decided to prepare a solution of that enzyme for testing the samples of peroxide examined.

For the estimation of catalase with peroxide Rosenblum[1] suggests (*a*) that the peroxide has to be buffered, and (*b*) that titanous chloride is the only suitable reagent for the titration of peroxide in presence of catalase.

In view of this statement, a number of peroxide preparations were tested by titration with titanous chloride, and the results were checked (1) by titration with potassium permanganate and (2) by titrating with sodium thiosulphate solution the iodine liberated by the peroxide from potassium iodide. In the tests with titanous chloride it was found that 0·5 ml. of a 0·04 per cent. solution of methylene blue gave a very satisfactory end-point if the dyestuff was added near the end of the titration, *i.e.* when the orange colour had faded to pale yellow.

By the courtesy of various manufacturers eight stabilised peroxide preparations and three not stabilised were obtained. No attempt was made to investigate the stabiliser present, apart from titrating the peroxides for acidity and ascertaining whether the stabiliser was organic or inorganic. The results of the tests on these eleven samples are given in Table I.

TABLE I

Hydrogen peroxide preparation (100 ml.)	Acidity to methyl orange, $N/10$ sodium hydroxide required ml.	A Permanganate, $N/10$ ml.	B Thiosulphate, $N/10$ ml.	C Titanous chloride, $N/10$ ml.	Difference A–C ml.
1. Stabilised by inorganic substance	2·4	18·0	17·95	17·35	0·65
		18·0	18·0	17·4	0·6
2. Stabilised by organic substance	4·0	18·5	18·5*	18·4	0·1
		18·5	18·5	18·4	0·1
3. Stabilised by sulphuric acid ..	10·0	15·95	16·0	15·3	0·65
		16·0	16·0	15·3	0·7
4. Stabilised by sulphuric acid ..	10·0	18·8	18·8	18·4	0·4
		18·8	18·8	18·4	0·4
5. Stabilised by inorganic substance	2·4	17·2	17·2	17·0	0·2
		17·2	17·2	17·0	0·2
6. Stabilised by organic substance	neutral	17·7	17·7	17·3	0·4
		17·7	17·7	17·3	0·4
7. Stabilised by organic substance	neutral	17·1	17·1	16·7	0·4
		17·1	17·1	16·7	0·4
8. Stabilised by organic substance	3·2	10·3	10·3*	10·1	0·2
		10·3	10·3	10·1	0·2
9. Not stabilised	2·4	14·7	14·7	14·7	nil
10. Not stabilised	neutral	17·3	17·3	17·3	nil
11. Not stabilised	3·2	19·0	19·0	19·0	nil

* Very slow liberation of iodine.

As is shown in Table I, the results of the permanganate and thiosulphate titrations agreed closely in every test whether the peroxides were stabilised or not. Where the stabiliser was organic and of a weakly acidic character, liberation of iodine was very slow and it was essential to use starch to obtain a satisfactory end-point; otherwise this was not necessary, for the change from yellow to white can be discerned by the eye, but not the slow return of yellow. The results of the titanous chloride titration agreed well with those obtained by titration with permanganate and thiosulphate for the three samples without stabilisers, but were invariably low when stabilisers were present.

It seemed incredible that with the sample (No. 3) in which the stabiliser was known to be sulphuric acid only, there should be this discrepancy between the potassium permanganate and titanous chloride titrations, but the determinations were kindly checked by Mr. J. H. Harwood, B.Sc., A.I.C.

As a further check, 0·05 ml. of 2 *N* sulphuric acid were added to 10 ml. of peroxide No. 10 and the mixture was diluted to 100 ml. There was no difference between the results obtained with permanganate and titanous chloride when the titrations were carried out at once or after 1 hour's standing, but after a week's standing the difference was as much as 1·0 ml. (Table II).

TABLE II

Hydrogen peroxide No. 10	Permanganate, *N*/10 ml.	Titanous chloride, *N*/10 ml.	Difference ml.
10 ml. + 0·05 ml. of 2 *N* sulphuric acid made up to 100 ml.	13·0	13·0	0·0
	13·0	13·0	0·0
10 ml. + 0·05 ml. of 2 *N* sulphuric acid made up to 100 ml. after standing 1 week	13·0	12·0	1·0
	13·0	12·0	1·0
10 ml. made up to 100 ml.	13·0	13·0	0·0
10 ml. made up to 100 ml. after standing 1 week	11·4	11·4	0·0

Attempts were made to ascertain if the titration could be completed by addition of permanganate after the required quantity of titanous chloride had been added; the methylene blue indicator was, of course, omitted. The results given in Table III show that this can be done.

TABLE III

Hydrogen peroxide		Permanganate, *N*/10 ml.	Titanous chloride, *N*/10 ml.	Difference ml.	Additional *N*/10 permanganate ml.
No. 2.	Original titration (as Table I)	18·5	18·4	0·1	—
,,	After 2 months	18·5	17·5	1·0	1·0
No. 3.	Original titration (as Table I)	16·0	15·3	0·7	—
,,	After 2 months	9·8	9·2	0·6	0·6
No. 4.	Original titration (as Table I)	18·8	18·4	0·4	—
,,	After 2 months	18·8	17·8	1·0	1·0

The sample of peroxide No. 2 after two months had not changed in titre to permanganate, but the original difference of 0·1 ml. between the titanous chloride and permanganate results had increased to 1 ml. A second test was made, the requisite quantity of titanous chloride was added, and the titration could be completed with permanganate. As the original permanganate titration agreed with the thiosulphate titration, it is obvious that the excess of permanganate solution, *i.e.* 1 ml. required over the volume of titanous chloride used, cannot be due to the stabiliser as such. The most likely explanation is that the stabiliser and some of the peroxide form a compound which is not easily reducible by titanous chloride, but is oxidised by a strong oxidising agent, such as permanganate. These results should throw some further light on the theory of stabilisation, a subject which is still much under discussion. Peroxide No. 3 had lost in strength, and the difference between the results of the permanganate and titanous chloride titrations had altered from 0·7 to 0·6 ml. The difference is too small to be of significance. The bottle containing No. 4 had not been opened often, and the sample had not lost strength at all, but here there was a notable increase in difference—from 0·4 ml. to 1 ml.

As titanous chloride is advocated for the standardisation of buffered hydrogen peroxide used in the titration of catalase, tests were carried out on buffered peroxide, B.D.H. Universal buffer and Clarke and Lubs's phosphate buffer being used. It will be seen from Table IV that here again the titanous chloride figures are low.

TABLE IV

Hydrogen peroxide No. 9	Permanganate, $N/10$ ml.	Titanous chloride, $N/10$ ml.	Difference ml.
25 ml. + 100 ml. of B.D.H. buffer, made up to 250 ml. ..	6·75 6·75	5·9	0·85
25 ml. + 100 ml. of Clarke & Lubs's sodium phosphate buffer, made up to 250 ml.	6·0 6·0	5·35	0·65

The preceding tests show therefore that titanous chloride is not a suitable reagent for the evaluation of hydrogen peroxide, but that titration with potassium permanganate and iodine liberation followed by titration with sodium thiosulphate are equally satisfactory. It was decided to use potassium permanganate in the estimation of catalase with hydrogen peroxide, as it was found that, at the strength used, an extract of liver did not decolorise the permanganate solution.

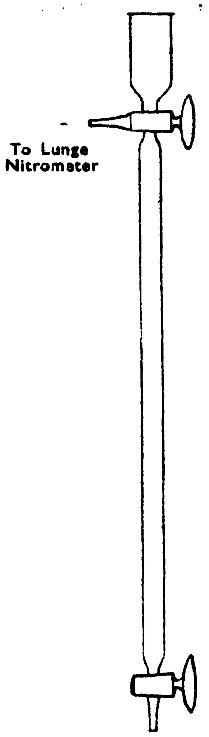
PART II

EFFECT OF CATALASE.—It is known that many substances inactivate catalase, notably sulphuric acid, persulphates and pyrogallol. It is reasonable to assume, therefore, that when a stabilised peroxide will not effervesce vigorously with dentures, etc., the stabiliser inactivates the catalase. This was found to occur with peroxides containing acids. With a weak solution of catalase there was hardly any liberation of oxygen. If the solution of catalase was very strong, oxygen could be evolved, despite the presence of acid. This explains why the same peroxide may be effective in the presence of pus, and yet practically useless as a mouthwash or for dentures. If the acid peroxides were first neutralised, inactivation of the catalase was avoided and oxygen was liberated freely, but if alkali was added to the hydrogen peroxide subsequent to the addition of catalase, no further oxygen was evolved, *i.e.* catalase had been permanently inactivated.

For the experiments to be described a solution of catalase was prepared from ½ lb. of fresh, minced calf's liver by leaving it overnight with 500 ml. of chloroform water in a refrigerator and filtering through muslin and filter-paper.

Rosenblum[1] prepared his solution of catalase by treating the aqueous liver extract with an equal volume of 95 per cent. alcohol to remove the proteins, the catalase remaining in solution, while Alyea and Pace[2] precipitated their catalase from solution with 95 per cent. alcohol, and used the precipitate, after purification by dissolving it in water, to obtain a solution of catalase. Although the methods appear contradictory, they are not so, because actually both the precipitate and the filtrate contain catalase; but I found the filtrate to be unsuitable. It has not been proved whether this is due to insufficiency of catalase or whether alcohol causes inactivation.

It was found that an extract prepared from fresh liver, as described above, gave better results than either of the solutions prepared by alcohol precipitation as just mentioned. It was necessary, however, so to adjust the concentration of the catalase solution that 1 ml., when added to a diluted (1 in 4) peroxide solution, would give a measurable rate of decomposition with most of the peroxides tested. If the catalase solution is very concentrated, even unsuitably stabilised hydrogen peroxides can usually be practically completely decomposed and give quantitative results. The aim here, however, was not to estimate the available oxygen, but to investigate the performance of hydrogen peroxide in presence of organic matter. By making a 1 in 10 solution of the liver extract a suitable catalase test solution was obtained; 0·1 ml. of this solution decomposed 0·03 g. of buffered hydrogen peroxide in 1 hour at laboratory temperature. The hydrogen peroxide was added in excess and back-titrated with permanganate.



METHOD.—Attempts were made to decompose the peroxide with catalase in a Schrödter apparatus and to collect the liberated oxygen over mercury in a Lunge nitrometer, but this was not found satisfactory, as decomposition was most erratic. The use of a narrow-bore tube (capacity about 8 ml.) for the decomposition enabled the reaction to proceed smoothly (Fig. 1). The tube was first evacuated by the use of a Lunge nitrometer containing mercury, and 1 ml. of undiluted peroxide was drawn in. This was followed by 3 ml. of water, with repeated evacuation; by putting the tube under vacuum, practically 1 ml. of catalase solution could be just drawn in when equilibrium with outside pressure was reached. The connection between the reaction tube and the nitrometer was opened, the levelling tube was lowered, and the mercury was kept at the level of the 30-ml. mark of the measuring tube. After 3 minutes, and again after 6 minutes, the connection with the reaction tube was closed for a few seconds while the volume of gas was read. (It is useful to have a half-time period of measuring the volume of gas, as this shows the course of the reaction more plainly.) Table V shows that peroxide preparations, whether stabilised or not, vary enormously in their reaction with organic matter.

Peroxides Nos. 3 and 4, which contained acid, decomposed only partly and very slowly. Nos. 1, 2 and 5 all decomposed quickly with catalase solutions. Nos. 6 and 7, which had good keeping properties, were indeed very suitably stabilised; even with a very weak catalase solution they decomposed with explosive violence. No. 8 decomposed steadily and completely, but rather slowly. No. 9, though not stabilised and of not very high acidity, must have contained traces of substances

which inactivate catalase, possibly persulphuric acid. No. 10 also contained minute traces of inhibitors, but No. 11 decomposed instantaneously, despite an acidity higher than that of No. 9.

TABLE V

THE REACTION OF HYDROGEN PEROXIDE WITH A SOLUTION CONTAINING CATALASE

Hydrogen peroxide preparation (100 ml.) No.	Acidity to methyl orange, $N/10$ sodium hydroxide required ml.	Remarks on the reaction	Volume of oxygen		Volume of available oxygen, by permanganate titration ml.
			After 3 minutes ml.	After 6 minutes ml.	
1	2·4	Quick start, steady evolution	15	19	20·7
2	4·0	Rapid start, 15 ml. in 30 seconds	16	18·5	20·5
3	10·0	Practically no reaction	3	5	11·0
4	10·0	Very slow reaction	4	9	21·0
5	2·4	Very quick start	15	16	18·9
6	neutral	Instantaneous, 20 ml. in 2 seconds	20	20	19·8
7	neutral	Instantaneous, 20 ml. in 2 seconds	20	20	19·9
8	3·2	Rather slow, but consistently steady	8	10	11·5
9	2·4	Very slow and little reaction	5	8·0	8·6
10	Practically neutral	Fairly quick	11	14·5	14·9
11	3·2	Very rapid, 16 ml. in 10 seconds	16	19	21·3

It should be the aim of stabilisation to obtain maximum keeping properties without inhibiting catalase, and a test such as that described above may well be employed when choosing the stabiliser and when testing the suitability of peroxides for pharmaceutical purposes.

I wish to thank Mr. A. Wexler (Hackney Technical Institute) and Dr. P. F. R. Venables (South-East Essex Technical College, Dagenham) for facilities for carrying out this work.

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27, EXETER GARDENS
ILFORD, ESSEX
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The Presence of Leuco-anthocyanins in Criollo Cacao

BY THE LATE A. W. KNAPP, M.Sc., F.I.C., AND J. F. HEARNE, A.I.C.

(*Read at the Meeting, May* 3, 1939)

THE range of colours exhibited by sections of cacao seeds of the various botanical varieties is of considerable importance, as there is little doubt that the nature of the coloured bodies present in the original unfermented beans greatly influences the appearance of the manufactured products and is associated with important differences in flavour.

Colours of unfermented cacaos differ very much, and the cotyledons may range from the pure white of the Criollo variety, through the many shades of pink or purple of hybrids, to the deep purple of the Forastero. This distribution of colour appears to be directly related to the botanical variety, although the purple of the Forastero may dominate and conceal an interbreeding with Criollo. Microscopical examination of the cotyledons of unfermented "beans" shows clearly that the purple cells so typical of Forastero beans are quite absent from the pure Criollo variety.

Many investigations of this difference in colour between the two main varieties of cacao have been made, but the complexity of the problem and the unstable nature of many of the constituents of the beans have restricted definite progress. The problem has been further complicated by the fact that many of the earlier investigators directed their attention mainly to Forastero cacao and appear to have been unaware that the fermented beans of commerce show characteristics differing widely from those of the natural unfermented beans. This has led to considerable misunderstanding of the true character of cacao pigments, for during fermentation most of the isolated pigment cells are destroyed, and the diffused and changed purple pigments have been confused with the coloured compounds produced from the catechin and catechu-tannin present in the bean.

Whilst certain of the properties of the colour constituents have been recognised for some time, little has been known of their actual constitution. The position has been clarified by Fincke[1] and by Knapp,[2] who have independently expressed the opinion that the alcohol-soluble pigment of Forastero cacao is an anthocyanin. This view has been confirmed and established by Robinson *et al.*,[3] who report that cacao beans contain cyanidin-3-monoside. No indication of the botanical variety of the beans examined is given in their paper, but as one of us (A. W. K.) selected and submitted them, we are able to state that they were authentic specimens of purple unfermented beans of the species *Forastero amelonado*, and were obtained from the Gold Coast. The exact nature of the sugar residue has yet to be determined. The importance of this new knowledge cannot be over-estimated. It can now be definitely stated that the colour of the fresh cacao bean is due to anthocyanin pigments, and these are no longer to be confused with the tannin and the catechin bodies and their oxidation and condensation products. It should now be possible to trace this one particular class of pigment substances through the various stages of the fermentation and manufacturing processes.

The genetics of cacao colour have been studied by Wellensiek[4] and by Pound.[5] Wellensiek has shown that the colour of the bean depends on genetic factors, and Pound has attempted to correlate bean colour, pod colour and flush colour, *i.e.* the colour of the young leaves.

With our fuller present knowledge of the anthocyanin character of the Forastero pigments, much more precise botanical investigation of this type should now be possible, and the distribution of colour in the various parts of the plant, such as the flowers, young leaves, pod tissues, etc., can now be studied in greater detail.

As a preliminary step in this direction, a detailed examination of a Criollo pod has therefore been carried out, attention being directed to the various tissues of the pod wall itself, in addition to those of the seeds.

Considerable care has been taken in the selection of the material for examination and with the Criollo cacao advantage was taken of the air-mail services to allow an examination to be made while the pod was in a fresh condition.

EXPERIMENTAL

Work in this laboratory has shown that, on vigorous treatment with strong hydrochloric acid, white Criollo beans yield a solution of brownish-red substances which exhibit in some degree reactions resembling those of the anthocyanins. Fincke[6] has already published a similar observation. The resemblance between these reactions and those of the anthocyanins is, however, of a general nature only, and our experiments have shown that a complex mixture of such coloured bodies exists in these acid solutions.

Solutions of this type have been prepared from the various components of a Criollo pod, and the colour reactions of certain purified pigments have been compared with those of a solution of cyanidin chloride prepared from unfermented Forastero cacao beans.

FORASTERO CACAO.—Selected Gold Coast pods of the species *Forastero amelonado* were gathered, and the beans were extracted immediately, in order that they should have undergone as little change as possible. An initial attempt was made to dry them directly in the sun, but, owing to the hygroscopic nature of the pulp, the drying was delayed. It was found necessary to wash off much of the adhering pulp before drying could be satisfactorily completed. The beans presented an entirely unfermented appearance. From these, for purposes of comparison, a solution of cyanidin chloride was prepared as follows:

The shell and germs were removed and 20 g. of the coarsely-ground cotyledons were extracted for two hours with 200 ml. of cold 1 per cent. hydrochloric acid. The extract was filtered with the aid of a pressure pump, and the resulting deep red solution was boiled for five minutes with one-quarter of its bulk of conc. hydrochloric acid, in order to hydrolyse the anthocyanin pigment. The mixture was then transferred to a separating funnel, and the liberated cyanidin chloride was extracted with small amounts of amyl alcohol, the total volume of amyl alcohol amounting to 50 ml. This alcoholic solution was withdrawn and repeatedly washed with water and with 1 per cent. aqueous hydrochloric acid. A large excess of benzene was then added, together with 30 ml. of 1 per cent. hydrochloric acid to take up the precipitated cyanidin chloride. More amyl alcohol was added to extract the pigment from the aqueous acid solution, and the purification processes were repeated. Finally the pigment was taken up in 50 ml. of 0·5 per cent. hydrochloric acid to obtain the solution of cyanidin chloride for use as the basis of reference.

CRIOLLO CACAO.—A pod of the Criollo type, having the "Old Red Ceylon" characteristics, was selected in Ceylon, at our request. The pod was packed in charcoal chips and immediately despatched by air-mail service to England, where it arrived 8 days later.

Little visible change had occurred, and the pod, which appeared to be just ripe, was in good condition on arrival. The beans, which were loosely assembled in the partly dried pulp, were immediately held in water at 90° C. for 10 minutes to destroy the oxidising enzymes and so stabilise the tannin constituents. None of the beans showed any trace of purple; they were all nearly pure white in cross section, and were thus truly representative of the Criollo variety.

Examination of the Criollo Beans.—The "stabilised" beans were shelled, the germs (radicles) were removed, and 20 g. of the coarsely-ground cotyledons were boiled for 30 minutes with 200 ml. of 1 per cent. hydrochloric acid. Little change was observed during the first 10 minutes, the solution remaining quite colourless. Continued boiling, however, resulted in the gradual development of a very pale orange colour. The resulting solution was filtered, sufficient conc. hydrochloric acid was added to increase the acid concentration to 5 per cent., and the solution was further concentrated by boiling. A dark brownish-red solution was quickly obtained, and a quantity of brown material was thrown out of solution.

The mixture was transferred to a separating funnel and extracted with successive small amounts of amyl alcohol, amounting in all to 50 ml. The orange-coloured aqueous layer was withdrawn, and the pigment in the amyl alcohol layer was purified in the manner described above for Forastero cacao. Sufficient 0·5 per cent. hydrochloric acid was finally added to take up the pigment and to give a solution of similar intensity in colour to that of the solution of cyanidin chloride prepared as described above from Forastero cacao.

Comparison was then made between the colour reactions of this purified solution and those of the solution of cyanidin chloride prepared from the Forastero beans. The tests were carried out in the manner outlined by G. M. and R. Robinson[7] for the examination of the anthocyanidins.

These tests included the colours of the solutions in 0·5 per cent. hydrochloric acid, the reactions with sodium acetate, ferric chloride and 10 per cent. sodium hydroxide solution, and the "oxidation" test showing the degree of recovery of the pigment on re-acidification after shaking with air and 10 per cent. sodium hydroxide solution.

Other solutions were prepared by re-precipitating the pigments from the solution in 0·5 per cent. hydrochloric acid, and re-dissolving them in 0·1 per cent. hydrochloric acid, and the colour reactions of these solutions were further characterised by a study of the colours given in solutions of graded *p*H values, as suggested by Robertson and Robinson.[8]

Examination of other Components of the Criollo Pod.—A similar development of brownish-red bodies was observed on prolonged boiling of other parts of the pod, such as the inner pod wall, the seed coatings, etc., with 10 per cent. hydrochloric acid. Each component was therefore examined in detail, the initial extraction in each case being as follows:

(*a*) *The seed coatings.*—The seed coatings were removed from the cotyledons, swilled with water to remove extraneous pulp and pulp juices, and extracted with boiling 1 per cent. hydrochloric acid. Little colour developed during this first extraction, but, on increasing the acid-content of the filtered extract to 5 per cent. and boiling for 15 minutes, brownish-red substances were produced.

(*b*) *The radicle.*—The amount of material furnished by the white "germs" of all the beans in the pod was so small that it was not possible to carry out so detailed an examination as with the other components. For this reason the preliminary extraction with 1 per cent. hydrochloric acid was omitted, and a direct extraction with 20 ml. of 15 per cent. hydrochloric acid was made. The red-brown pigments were quickly obtained and extracted directly with 20 ml. of amyl alcohol.

(*c*) *The placenta.*—The whole placenta was air dried, coarsely ground and extracted in the same way as the seed coatings.

(*d*) *The inner membrane of the pod wall.*—The soft pulpy lining of the pod wall was peeled off and extracted directly with 1 per cent. hydrochloric acid. Although this material was greyish, with a trace of purple, the extracts obtained on boiling with the 1 per cent. hydrochloric acid were almost colourless. After filtration the acid concentration was increased to 5 per cent., and the solution was boiled until the deep brownish-red colour had fully developed.

(*e*) *The pod wall.*—Sections of the inner portions of the soft yellowish-white pod wall were carefully removed and cut into thin slices, and 20 g. of this material were extracted for 30 minutes with 200 ml. of boiling 1 per cent. hydrochloric acid. The solution, which at this stage had a very pale orange colour, was filtered with difficulty, and the acid concentration was increased as before to develop the red substances.

Each of the coloured acid solutions so obtained was then extracted with amyl alcohol, and the pigments in the alcoholic solution were purified as previously described. Finally the pigment was dissolved in 0·5 per cent. hydrochloric acid, and the colour reactions were observed.

(*f*) *The coloured external skin of the pod.*—From our previous experience with Forastero pods it had been expected that on direct extraction with cold dilute hydrochloric acid, the red outer skin of the Criollo pod would yield a solution of anthocyanin colour. This, however, was not found to be so with this particular pod.

SUMMARY OF RESULTS.—The solution of the purified pigment extracted from the cotyledons of the unfermented Criollo beans gave colour reactions identical with those given by the solution of cyanidin chloride prepared, as described above, from Forastero cacao. This agreement in colour reactions also applied to the purified pigments obtained from the seed coatings, the radicles, the placenta and the inner lining of the pod wall.

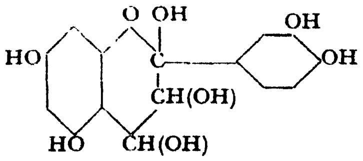
The reactions exhibited by the pigment isolated from the pod wall closely resembled those of the cyanidin chloride solution from the Forastero beans, although certain differences were observed in the ferric chloride reactions. It was thought however, that these slight discrepancies were probably due to the presence of contaminating substances which had not been removed during the purification process, rather than to any difference in the pigments themselves.

Each component of the Criollo pod examined contained, therefore, colourless bodies which yielded, on vigorous treatment with strong hydrochloric acid, a solution containing a mixture of brownish-red bodies. From each of these mixtures, with the possible exception of that from the main pod wall, a purified solution of cyanidin chloride has been separated.

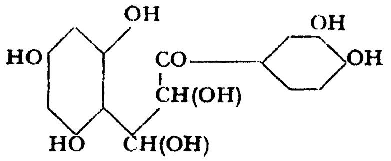
The nature of the other coloured substances developed by the strong acid treatment has not been determined. They are not, however, anthocyanin pigments.

CONCLUSION.—*The Nature of the Colourless Precursor of the Anthocyanin Pigment.*—The experiments detailed above have shown that in practically all the parts of the seed and fruit of Criollo cacao there are present certain colourless substances which may be extracted with 1 per cent. hydrochloric acid to yield practically colourless solutions. On increasing the acid-content, either directly or by prolonged boiling, brownish-red bodies are developed, one of which has been shown to be cyanidin chloride. These facts indicate that Criollo cacao contains a leuco-anthocyanin which, on treatment with strong acid, yields cyanidin chloride.

The nature of the leuco-anthocyanins has been studied by G. M. and R. Robinson,[9] who suggest that the immediate precursor of cyanidin, as shown in formula I, is a ring structure tautomeric with that shown in formula II.



I



II

It is probable that these leuco bodies in the various tissues of the Criollo cacao pod are present in the form of glycosides.

This discovery may be of use to botanists, especially if the proportionate amounts of leuco-anthocyanin and anthocyanin are related to the extent of interbreeding of Criollo and Forastero varieties.

We wish to thank Mr. H. Nicholas, of the Gold Coast Agricultural Department, for preparing the Forastero beans, and the Anglo-Ceylon and General Estates Co., Kandy, for the Criollo pod. We also thank Messrs. Cadbury Brothers for permission to publish this paper.

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CHEMISTS' DEPARTMENT
MESSRS. CADBURY BROS., LTD.
BOURNVILLE

January 18*th*, 1939

DISCUSSION

Professor HILDITCH remarked that he had been very interested in Mr. Hearne's description, and asked if colourless leuco-anthocyanins had been isolated in a purified form? He was interested in the possibility of natural leuco-anthocyanins possessing antioxidant properties, since it had recently been observed that concentrates of natural antioxygenic compounds prepared from seed endosperms were basic in character, and lost their power of retarding oxidation in fats after they had been neutralised with a mineral acid.

Mrs. TRITTON asked if the cyanidin chloride could be obtained from the beans in a crystalline state. Also, was it possible to make a quantitative colorimetric estimation of the anthocyanins?

Dr. J. G. A. GRIFFITHS asked if the identity of cyanidin chloride with the product of hydrolysis from Criollo beans had been established by spectroscopic examination.

Dr. H. E. COX expressed surprise at the extraordinary colour change shown to occur between *p*H 12 and *p*H 13 and enquired the cause.

Mr. HEARNE, replying, said that he had not actually isolated leuco-anthocyanins in a pure form. From the fact that the cacao butter itself in chocolate was a particularly stable fat he thought that one might infer that antioxidant substances were present. He had not prepared pure cyanidin chloride from Forastero beans. So far as he knew, the method suggested by Mrs. Tritton for the direct colorimetric estimation of the purple pigment might be feasible, but it had not been found practicable in this particular instance. Spectroscopic methods of examination had not been tried. In reply to Dr. Cox the author said that apparently when *p*H 12 was passed some decomposition occurred and there was a pronounced change; moreover, beyond that *p*H value the colour was not stable.

Studies in the Analytical Chemistry of Tungsten: I

BY D. A. LAMBIE, B.Sc., A.I.C.

ALTHOUGH tungsten is one of the best known and most widely used of the "rarer" elements, its analytical chemistry is a difficult subject, which still leaves room for a great deal of improvement. This is due to the idiosyncrasies of the element, *e.g.* its power of complex-formation with a number of elements; it differs from molybdenum and the heavy metals in not reacting quantitatively with the sulphide ion, and from the "earths," in not being precipitated from organic acid solution by tannin or cupferron. This behaviour may be modified by its association with other elements, induced partial precipitation taking place. The detection of small quantities of tungsten and the polytungstic and heteropolytungstic acids also offer a promising field for further analytical investigation.

Having from time to time encountered difficulties in my practical experience of tungsten analysis, I have set myself the task of critically surveying the subject, and of communicating such results as may be of interest or practical value in a series of papers under the above general title.

I. THE RECOVERY OF TUNGSTEN FROM SULPHATE SOLUTIONS

The recovery of tungsten from sulphate solutions is of great practical interest in its bearing on the separation of tungsten from molybdenum. The most reliable and most convenient method for effecting the separation consists in the precipitation of molybdenum sulphide from tartrate solution, tungsten passing into the filtrate. The quantitative recovery of tungsten from the tartrate solution, however, is admittedly not so simple as that of molybdenum.[1] It involves removal of the tartaric acid, and this is most readily effected by heating with nitric and sulphuric acids; the product is a solution containing sulphuric acid and sodium sulphate (from the alkali added prior to the sulphide precipitation). It is the recovery of tungsten from such solutions that formed the object of this investigation.

The following are the recognised precipitants for tungstic acid: (1) mineral acids, (2) mercurous nitrate, (3) organic bases or alkaloids, and (4) tannin and cinchonine. It was decided to study the effect of sulphuric acid and alkali sulphate on procedures utilising these reagents.

(1) MINERAL ACIDS.—Alkali sulphate is known to have an adverse effect on the precipitation of tungstic acid; thus Hillebrand and Lundell[2] state that "alkali salts prevent complete precipitation of tungsten by digestion with acids." I ascertained that a melt containing 0·05 g. of tungstic oxide, 0·5 g. of potassium bisulphate, and 5 ml. of strong sulphuric acid, when leached with water, gave a faintly turbid solution, which cleared on boiling. This confirms the observations of Powell, Schoeller and Jahn,[3] who reject bisulphate as a means for separating titanium from tungsten. With 0·1 g. of tungstic oxide, 1 g. of bisulphate and 10 ml. of strong sulphuric acid the solution was initially turbid; continued boiling caused hydrolysis, a flocculent yellow precipitate being formed.

Two solutions of sodium tungstate were prepared from carefully purified tungstic oxide, 0·5010 g. and 0·5001 g. being heated with 1 g. portions of sodium carbonate and a few ml. of water in porcelain dishes. The solutions were made up to 500 ml., and the tungstic oxide was determined in 20-ml. portions by (1) precipitation with hydrochloric acid and cinchonine, and (2) Schoeller and Jahn's tannin-cinchonine method.[4]

Solution A:	Method (1).	Found 0·0201 g.	Calculated 0·02004 g.
,, A:	,, (2).	,, 0·0202 g.	,, 0·02004 g.
,, B:	,, (2).	,, 0·0200 g.	,, 0·0200 g.

The values adopted were 0·0201 g. and 0·0200 g., respectively.

The use of sulphuric acid as a precipitant was first investigated. Aliquot portions of sodium tungstate solution were taken in 600-ml. beakers, and varying amounts of strong sulphuric acid and anhydrous sodium sulphate were added. In Expts. Nos. 1 and 2 Margueritte's method[5] was used; the mixture was evaporated until copious fumes of sulphuric acid were evolved, 3 ml. of strong nitric acid were added to re-oxidise any reduced tungstic oxide, and the mass was treated with 40 ml. of water. In Expts. Nos. 3 to 5, after evaporation until sulphuric acid fumes appeared and oxidation with a few drops of nitric acid, the cold mass was taken up with 200 ml. of water and the solution was digested for an hour at boiling-point on a hot plate. In every instance the precipitate was allowed to stand overnight before filtration. The precipitated tungstic acid was collected on a filter-paper of fine texture, having in its apex a pad of filter-pulp, and then washed with 5 per cent. v/v sulphuric acid, ignited and weighed. Without exception the filtrates were clear and remained so on standing. The results are given in Table I.

TABLE I

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Added
1	0·0201	0·0190	−0·0011	10 ml. of sulphuric acid
2	0·0201	0·0185	−0·0016	10 ,, ,, ,, ,, and 5 g. of sodium sulphate
3	0·0200	0·0190	−0·0010	10 ,, ,, ,, ,,
4	0·0200	0·0183	−0·0017	10 ,, ,, ,, ,, and 10 g. of sodium sulphate
5	0·0020	nil	−0·0020	10 ,, ,, ,, ,, ,, 5 g. ,, ,, ,,

These results show that the use of sulphuric acid as a precipitant leads to negative errors, which may be proportionately large with small amounts of tungstic acid. As was expected, the presence of alkali sulphate increased the magnitude of the negative error.

Experiments were next made with *aqua regia* as precipitant. Aliquot portions of the sodium tungstate solution were taken in 600-ml. beakers, and varying quantities of sulphuric acid and of anhydrous sodium sulphate, dissolved in a little water, were added. The solutions, measuring about 100 ml., were treated with 40 ml. of strong hydrochloric acid and 15 ml. of strong nitric acid and evaporated to about 50 ml.; five ml. more of strong nitric acid was added and the volume was reduced to 5 to 10 ml. With the larger amounts of sodium sulphate, evaporation was interrupted when the volume had reached 10 to 15 ml. to avoid loss by spurting. Hot water was added to bring the volume to 150 ml., and the solution was heated for half-an-hour on a hot plate.

After standing overnight the precipitated tungstic acid was collected, washed with 1 per cent. v/v hydrochloric acid, ignited and weighed. The filtrates were perfectly clear. In Expts. Nos. 6 to 10 (Table II) the recovery was incomplete. In 11 and 12, an attempt was made to recover the tungsten by adding 5 ml. of 5 per cent. cinchonine solution after the dilution with water, but all the tungstic acid remained in solution.

TABLE II

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Added	
6	0·0200	0·0195	−0·0005	5 g. of sodium sulphate	
7	0·0200	0·0195	−0·0005	10	
8	0·0200	0·0155	−0·0045	20 ,, ,, ,, ,,	
9	0·0200	0·0191	−0·0009	10 ,, ,, ,, ,,	and 5 ml. of sulphuric acid
10	0·0020	0·0004	−0·0016	5 ,, ,, ,, ,,	
11	0·0020	nil	−0·0020	5 ,, ,, ,, ,,	Cinchonine added after dilution
12	0·0020	nil	−0·0020	10 ,, ,, ,, ,,	
13	0·0020	nil	−0·0020	10 ml. of sulphuric acid after fusion with potassium bisulphate	
14	0·0230	0·0224	−0·0006		
15	0·0524	0·0517	−0·0007		
16	0·1023	0·1016	−0·0007		

In Expts. Nos. 13 to 16, tungstic oxide was fused in a vitreosil crucible with 0·5 g. of potassium bisulphate, and the cooled melt was re-heated with 10 ml. of strong sulphuric acid until fluid. The solution, when cold, was transferred to a 600-ml. beaker containing water, and the crucible was rinsed with water. The solution (about 200 ml.) was boiled for half-an-hour to precipitate the tungstic acid, filter-pulp and 5 ml. of 5 per cent. cinchonine solution being added. After standing overnight the precipitate was collected, ignited and weighed as before.

These results demonstrate that acid precipitation as a general method for the recovery of tungstic acid from sulphate solution is unreliable even with the addition of cinchonine, as variable negative errors are always incurred.

(2) MERCUROUS NITRATE.—When tungstic acid is precipitated by mercurous nitrate from sulphate solution, mercurous sulphate is co-precipitated, hence a large excess of precipitant is required; the precipitate becomes inconveniently bulky and tends to retain alkali, which contaminates the ignited oxide. Moreover, the ignition of large precipitates of mercury salt is a risky operation. These considerations justify the rejection of mercurous nitrate as a precipitant for tungstic acid from sulphate solutions.

(3) ORGANIC BASES AND ALKALOIDS.—The insolubility of benzidine sulphate renders that base unsuitable for the present purpose.

Cinchonine is by far the most widely used organic precipitant for tungsten; but it has always been recognised that, in presence of alkali salt, complete precipitation occurs only after long standing (Cremer gives 48 hours[6]). It was to be expected, therefore, and has been fully confirmed by Expts. Nos. 17 to 21 (Table III), that alkali sulphate prevents complete precipitation by cinchonine.

In Expt. No. 17, an aliquot volume of sodium tungstate solution was taken, whilst in Expts. Nos. 18 to 21, tungstic oxide was fused with 0·5 g. of potassium bisulphate and the quantity of sulphuric acid given in the Table; the fused mass was leached, and the solution was treated with excess of cinchonine reagent and set aside overnight before filtration.

TABLE III

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Conditions
17	0·0020	0·0008	−0·0012	10 g. of sodium sulphate added
18	0·0113	0·0089	−0·0024	Re-fused with 5 ml. of sulphuric acid
19	0·0236	0·0221	−0·0015	,, ,, 5 ,, ,, ,, ,,
20	0·0215	not weighed	—	,, ,, 10 ,, ,, ,, ,,
21	0·0120	,, ,,	—	,, ,, 10 ,, ,, ,, ,,

In Expts. Nos. 20 and 21, the solution of the melt was clear. Addition of cinchonine produced no precipitate, and even after a week's standing only a very small precipitate was formed, hence these tests were discarded. Two tests made with other alkaloids (quinine and nicotine) proved discouraging, so that this line of investigation was abandoned.

(4) TANNIN AND CINCHONINE.—This method was developed by Schoeller and Jahn[4] to recover small amounts of tungstic acid from solutions containing considerable amounts of alkali chloride which, far from being inimical to the precipitation, was found to assist flocculation.

In Expts. Nos. 24 to 30 (Table IV) aliquot portions of sodium tungstate solution were taken, and varying amounts of sodium sulphate or sulphuric acid were added. The solution, diluted to about 200 ml., was made feebly alkaline with ammonia, heated to 50° C. and treated with a solution of 0·5 g. of tannin. Dilute hydrochloric acid was then added until the solution was acid to litmus, and pulped filter-paper and 5 ml. of 5 per cent. cinchonine solution were stirred in, the stirring being prolonged until a thorough incorporation of precipitate and pulp was achieved. The beaker was set aside to cool (in running water to expedite cooling), and the precipitate was collected on a Whatman No. 41 filter, washed thoroughly with ammonium chloride solution containing cinchonine, ignited and weighed.

In Expts. Nos. 31 to 33, the tannin-cinchonine method was applied to the filtrates from the precipitates obtained in Expts. Nos. 3, 4 and 9 (Tables I and II); the entries under "Tungstic oxide taken" reproduce the negative errors incurred in the earlier experiments. As will be seen under "Tungstic oxide found," recovery was complete.

TABLE IV

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Added
24	0·0201	0·0203	+0·0002	20 g. of sodium sulphate and 10 g. of ammonium chloride
25	0·0201	0·0202	+0·0001	40 g. of sodium sulphate and 10 g. of ammonium chloride
26	0·0020	0·0020	nil	—
27	0·0020	0·0021	+0·0001	40 g. of sodium sulphate
28	0·0020	0·0020	nil	20 ml. of sulphuric acid
29	0·0200	0·0202	+0·0002	40 g. of sodium sulphate
30	0·0200	0·0203	+0·0003	20 ml. of sulphuric acid
31	0·0010	0·0011	+0·0001	—
32	0·0017	0·0018	+0·0001	—
33	0·0009	0·0015	+0·0006	—

A few experiments were made to determine the applicability of this method to the recovery of tungstic acid from the solution of a potassium bisulphate melt in ammonium carbonate.

Tungstic oxide was fused with ten times its weight of potassium bisulphate in a vitreosil crucible. The cold melt was leached with 1 g. of ammonium carbonate dissolved in a little water, the crucible being warmed gently on the hot plate to facilitate solution. The liquid was transferred to a beaker, 50 ml. of 20 per cent. ammonium chloride solution were added, and the volume was made up to about 200 ml.; after heating to about 50° C., 0·5 g. of tannin dissolved in a few ml. of water was added (for more than 0·05 g. of tungstic oxide a weight of tannin equal to ten times that of the tungstic oxide was used), followed by dilute hydrochloric acid until the solution was acid to litmus. A cream of pulped filter-paper and 5 ml. of 5 per cent. cinchonine solution added drop-wise were stirred in, and the determination was completed as in the previous series. The results are given in Table V.

In the first two tests (34 and 35) the solutions were filtered hot (35 after standing for two hours on the boiling water-bath), and, as will be seen, gave negative errors. This was no doubt due to the cinchonine tannate remaining in solution at higher temperatures, and so failing to cause precipitation of the colloidal tungsten-tannin complex.

The other tests, in which the solution was allowed to stand until cold before filtration, showed good recovery.

TABLE V

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.
34	0·0065	0·0056	−0·0009
35	0·1014	0·0996	−0·0018
36	0·0256	0·0254	−0·0002
37	0·1053	0·1052	−0·0001
38	0·0518	0·0516	−0·0002
39	0·0109	0·0108	−0·0001
40	0·0050	0·0051	+0·0001
41	0·1000	0·0998	−0·0002
42	0·0506	0·0508	+0·0002

In a further series of experiments (Table VI) the bisulphate melt was leached with water, the crucible was rinsed with dilute ammonia, and the solution was rendered alkaline with ammonia. From this point the precipitation was carried out as in the preceding tests. In Expts. Nos. 53 to 59, after fusion with potassium bisulphate, the cold melt was re-fused with 10 ml. of strong sulphuric acid. This melt, containing a large excess of sulphuric acid, was leached with water and ammonia to give an alkaline solution, and the tungstic acid was precipitated as described above.

The experiments provide ample evidence that the tannin-cinchonine method achieves a quantitative recovery of tungstic acid from solutions containing considerable amounts of alkali sulphate.

It is possible by the tannin-cinchonine method to treat solutions containing not more than 0·2 g. of tungstic oxide. Larger amounts of tungstic oxide would result in inconveniently large precipitates, with attendant difficulties of filtration and washing. Under such conditions one of two alternative procedures may be adopted:—(*a*) the solution may be made up to a convenient volume and an aliquot portion taken containing less than 0·2 g. of tungstic oxide; (*b*) the bulk of the tungstic acid may be precipitated by means of acid, and the balance recovered from solution, after filtration, by the tannin-cinchonine method.

TABLE VI

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.
46	0·0213	0·0216	+0·0003
47	0·0527	0·0528	+0·0001
48	0·1031	0·1028	−0·0003
49	0·0128	0·0129	+0·0001
50	0·0256	0·0255	−0·0001
51	0·0008	0·0011	+0·0003
52	0·0028	0·0031	+0·0003
53	0·0013	0·0016	+0·0003
54	0·1006	0·1004	−0·0002
55	0·1015	0·1012	−0·0003
56	0·1006	0·1007	+0·0001
57	0·0512	0·0518	+0·0006
58	0·0512	0·0514	+0·0002
59	0·1016	0·1018	+0·0002

In order to explore the possibility of combining these last two operations, *i.e.* acid precipitation of the major and tannin-cinchonine precipitation of the minor fractions, three series of tests were made.

A. Effect of excess of acid on the precipitation of tungstic acid by tannin and cinchonine.—Aliquot portions of a sodium tungstate solution were taken, treated with 50 ml. of 20 per cent. ammonium chloride solution, diluted to 200 ml., and heated to about 50° C. A solution of 0·5 g. of tannin in a little water was added and followed by the stated volume of hydrochloric acid, filter-pulp, and 5 ml. of 5 per cent. cinchonine solution. When cold the precipitate was collected, washed, ignited and weighed.

The results recorded in Table VII (Expts. Nos. 60 to 65) show that complete precipitation of tungstic acid takes place in presence of an excess of 10 ml. of strong hydrochloric acid in a volume of 200 ml.

TABLE VII

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Strong hydrochloric acid added ml.
60	0·0501	0·0503	+0·0002	1
61	0·0501	0·0500	−0·0001	5
62	0·0501	0·0503	+0·0002	10
63	0·0501	0·0498	−0·0003	20
64	0·0501	0·0496	−0·0005	20
65	0·0501	0·0491	−0·0010	30

In the form in which the method was published by Schoeller and Jahn, the tannin is added to an alkaline tungstate solution which is then acidified. To render alkaline a solution containing a considerable quantity of precipitated tungstic acid would defeat the purpose of the acid precipitation; hence it was of interest to study the effect of adding tannin to the acid solution of tungstic acid.

That an essential difference exists is immediately apparent, for, on treating an alkaline tungstate solution with tannin followed by an excess of acid, a brown colour, or, with more than a few milligrams of tungstic acid a brown flocculent precipitate, results; on the other hand, if tannin is added to the clear acid solution containing even so much as 0·05 g. of tungstic acid, very little colour and no precipitate are produced (such a solution is obtained when 0·05 g. of tungstic acid is fused with 0·5 g. of potassium bisulphate and 5 ml. of strong sulphuric acid, the melt leached with water and the solution boiled). This fact should be borne in mind when tannin is used as a qualitative reagent for tungsten.

B. Tannin-cinchonine precipitation from acid solution.—A number of tests were made in which varying amounts of tungstic oxide were fused with potassium bisulphate and then re-melted with strong sulphuric acid. The final melt, which in general remained clear, was transferred to a beaker containing 100 ml. of water, the crucible was rinsed out, and the rinsings were added to the main solution. A clear solution was obtained on heating, except in the tests with 0·05 g. and 0·10 g. of tungstic oxide. The solution was diluted to 200 ml., heated to about 50° C., and treated with 0·5 g. of tannin dissolved in water, filter-pulp and (dropwise) 5 ml. of 5 per cent. cinchonine solution during vigorous stirring. Addition of the tannin produced no precipitate or change in colour, but on addition of the cinchonine a characteristic buff-brown precipitate was obtained immediately.

After cooling, the precipitate was filtered off, washed as before, ignited and weighed. In Expts. Nos. 66 to 70 (Table VIII) 5 ml. of strong sulphuric acid were added to the melt, and the recovery of tungstic acid was satisfactory regardless of whether ammonium chloride was added or not. With 10 ml. of strong sulphuric acid, however (Expts. Nos. 71 to 76), the recovery was not quite quantitative.

TABLE VIII

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.	Sulphuric acid added ml.	Ammonium chloride added g.
66	0·0503	0·0501	−0·0002	5	10
67	0·0047	0·0047	nil	5	none
68	0·0051	0·0052	+0·0001	5	10
69	0·0109	0·0109	nil	5	10
70	0·0121	0·0120	−0·0001	5	none
71	0·0517	0·0505	−0·0012	10	"
72	0·0239	0·0233	−0·0006	10	"
73	0·0008	0·0007	−0·0001	10	"
74	0·0085	0·0083	−0·0002	10	"
75	0·0212	0·0204	−0·0008	10	"
76	0·0538	0·0529	−0·0009	10	"

C. Combination of acid and tannin-cinchonine precipitations.—It was found that by boiling a solution such as was obtained in Expts. Nos. 71 to 76 (*i.e.*

containing 10 ml. of strong sulphuric acid) the bulk of the tungstic acid was precipitated if more than 0·02 g. was present.

Similar solutions were taken in Expts. Nos. 77 to 80 and boiled for half-an-hour, and the precipitation was completed with tannin and cinchonine, as described under B. When cold, the precipitate was collected, washed, ignited and weighed.

TABLE IX

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error g.
77	0·0202	0·0204	+0·0002
78	0·0528	0·0524	−0·0004
79	0·1032	0·1031	−0·0001
80	0·1030	0·1025	−0·0005

These three series of experiments prove that the precipitation with acid and tannin may be combined, provided that the final solution is not too acid. To verify this conclusion, a final series of experiments was made. In each test 0·5 g. of tungstic oxide was dissolved by heating with 1 g. of sodium carbonate and a few ml. of water. The resulting solution was treated in a 600-ml. beaker with the salts shown in Table X. The volume of the liquid was reduced to 30 or 40 ml. by heating on the hot plate, care being taken to avoid spurting when crystals separated; 30 ml. of strong hydrochloric acid were added, and the solution was boiled for a few minutes to precipitate yellow tungstic acid. The volume was brought to about 300 ml. by addition of hot water, and a solution of 0·5 g. of tannin together with filter-pulp, and 5 ml. of 5 per cent. cinchonine solution were added during thorough agitation. After cooling, the precipitate was collected on a filter of close texture, having filter-pulp in the apex, washed with the ammonium chloride and cinchonine solution, ignited and weighed. The tabulated results (Expts. Nos. 81 to 85) show a satisfactory recovery.

TABLE X

Expt. No.	Tungstic oxide taken g.	Tungstic oxide found g.	Error. g.	Added
81	0·5003	0·5004	+0·0001	5 g. of sodium sulphate
82	0·5013	0·5018	+0·0005	20 ,, ,, ,, ,,
83	0·5007	0·5011	+0·0004	20 ,, ,, ammonium sulphate
84	0·5013	0·5012	−0·0001	20 ,, ,, ,, ,,
85	0·5018	0·5115	−0·0003	20 ,, ,, sodium chloride

SUMMARISED DIRECTIONS FOR THE PRECIPITATION OF TUNGSTIC ACID.—The following technique was adopted in the course of several hundred tungsten determinations. In most instances the ore, which was free from interfering substances such as molybdenum, was decomposed with *aqua regia* to give a residue of tungstic acid and gangue. Treatment of this washed residue with ammonia (or sodium hydroxide followed by excess of ammonium chloride) and filtration provided a solution to which the tannin-cinchonine method could be applied.

Reagents.—Cinchonine solution: prepared by dissolving 50 g. of the alkaloid in 500 ml. of 1:1 hydrochloric acid, diluting to 1 litre with water and filtering.

Ammonium chloride and cinchonine washing solution:—100 ml. of a 20 per cent. ammonium chloride solution and 20 ml. of the above cinchonine solution are diluted to 1 litre with water.

I. In solutions containing not more than 0·2 *g. of tungstic oxide.*—Unless already alkaline, the solution is rendered so by addition of ammonium hydroxide and 50 ml. of 20 per cent. ammonium chloride solution are added, although this may be omitted if sufficient salts are already present. The solution is diluted to 200 ml., heated to about 50° C., and treated with a solution of 0·5 to 2 g. of tannin in a few ml. of water (tannin at least ten times the estimated weight of tungstic oxide should be added). Hydrochloric acid (1:1) is added, during agitation, until the solution is acid to litmus paper. The creamed pulp of half of a 9-cm. Whatman No. 41 filter-paper is added, followed by 5 ml. of the cinchonine solution added dropwise with continual stirring so as to incorporate the precipitated tungsten-tannin complex, filter-fibre and cinchonine tannate thoroughly. The beaker is set aside until cold or cooled in running water.

The precipitate is collected on a filter-paper of loose texture (Whatman No. 41) and washed three or four times with the ammonium chloride and cinchonine solution, the precipitate being churned up with the stream of liquid. The precipitate is returned to the beaker with the aid of a stream of wash-solution directed into the inverted funnel, stirred up with some wash-solution and re-filtered on the same paper, being transferred completely to the filter, and the washing is completed.

The filter and precipitate are ignited wet in a tared porcelain crucible, the final ignition being carried out over a Bunsen burner to give tungstic oxide, which should be of a good yellow colour. A green residue, which adheres to the crucible, may be obtained if, owing to incomplete washing of the precipitate, alkali salts are still present.

II. In solutions containing more than 0·2 *g. of tungstic oxide.*—An aliquot portion of the solution may be taken and the tungstic oxide precipitated as under *I*.

If it is desired to precipitate all the tungstic acid, the feebly acid or alkaline solution is cautiously evaporated to 30 or 40 ml. on a hot plate; 30 ml. of strong hydrochloric acid are added, and the solution is boiled so that the precipitated tungstic acid turns yellow. The solution is diluted to 300 ml. with hot water and treated with 0·5 g. of tannin dissolved in a little water, filter-pulp as described above, and 5 ml. of cinchonine solution added dropwise with vigorous stirring.

When cold, the liquid is filtered through a filter-paper of close texture (Whatman No. 40) having a pad of filter-pulp in the apex. The washing is carried out with ammonium chloride and cinchonine solution as in the previous method. Any white turbidity in the filtrate during the washing may be ignored, since a number of tests have proved it to be free from tungsten.

Should a pellicle of tungstic acid adhere firmly to the beaker, it may be dissolved in a few ml. of ammonium hydroxide and re-precipitated by the addition of a little tannin, hydrochloric acid, filter-pulp and cinchonine solution. It is convenient to do so before the bulk of the precipitate is rinsed back into the beaker for washing. The precipitate is ignited wet in a tared porcelain crucible and weighed as tungstic oxide (WO_3).

SUMMARY.—The recovery of tungstic acid from sulphate solutions containing alkali sulphate, by precipitation with mineral acid or cinchonine, is shown to be incomplete. The tannin-cinchonine method of Schoeller and Jahn provides a rapid and accurate means of recovering tungstic acid from such solutions. A modification of the same method, by which more substantial amounts of tungstic acid (more than 0·2 g.) can be determined, has been worked out.

In conclusion, I desire to record my indebtedness to Dr. W. R. Schoeller for his kindly interest and helpful criticism.

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An Improved Universal Buffer

BY W. C. JOHNSON AND A. J. LINDSEY, PH.D., A.I.C.

UNIVERSAL buffer solutions have been described by the following authors: Prideaux,[1] Prideaux and Ward,[2] Michaelis,[3] and Britton and Robinson.[4] The most satisfactory of these was the mixture recommended by Britton and Robinson. This solution, 0·0286 molar with respect to hydrochloric acid, citric acid, potassium dihydrogen phosphate, veronal and boric acid, acted as a buffer between *p*H 2·6 and 12·0, and titration with 0·2 *N* sodium hydroxide solution gave a change of *p*H which was rectilinear between the values of 4 and 8. A solid mixture, containing no hydrochloric acid and having the advantage of portability and small storage space, was recommended to serve the same purpose. This mixture was dissolved and titrated either with sodium hydroxide for *p*H values over 3·91 or with hydrochloric acid for lower values.

We have effected a simplification by preparing a solid mixture, using free diethylbarbituric acid instead of the sodium salt employed by Britton and Robinson. It is thus possible to prepare buffer solutions of any *p*H between 2·6 and 12·0 by titrating a solution of this mixture with 0·2 *N* sodium hydroxide solution. Citric acid (6·008 g.), potassium dihydrogen phosphate (3·893 g.), boric acid (1·769 g.) and diethylbarbituric acid (5·266 g.) form the solid mixture which, when dissolved in water and made up to one litre, is ready for use. All the chemicals employed were of analytical reagent quality, with the exception of the diethylbarbituric acid which conformed with the B.P.C. standard.

The *p*H values of mixtures of 100 ml. of the solution with various quantities (x_1) of 0·2 *N* sodium hydroxide solution free from carbonate, were determined at

18° C. A hydrogen electrode[5] connected by means of a saturated salt bridge with a saturated calomel half-cell was employed for this purpose, and the potentials were measured with either a Cambridge or a Tinsley potentiometer. A further series of measurements (x_2) was made upon mixtures after dilution to a constant volume of 200 ml. As was expected, the results agreed well with those of Britton and Robinson, but results up to 0·1 *p*H lower were obtained between *p*H 7·5 and 8·5. Further, values a little higher than those of Britton and Robinson were obtained between *p*H 2·6 and 4·0. The linear equation, $pH = 0{\cdot}0853x + 2{\cdot}686$ holds accurately over the range from *p*H 4 to *p*H 7·5, and more approximately (within 0·1 *p*H) over the wider range to *p*H 9·0. For values outside this range quantities taken from the table below should be employed. The table showing even increments in *p*H was constructed by interpolation from the results of the titrations.

*p*H	x_1	x_2	*p*H	x	*p*H	x
2·6	2·0	0·0	5·8	36·5	9·0	72·7
2·8	4·3	2·4	6·0	38·9	9·2	74·0
3·0	6·4	5·0	6·2	41·2	9·4	75·9
3·2	8·3	7·3	6·4	43·5	9·6	77·6
3·4	10·1	9·3	6·6	46·0	9·8	79·3
3·6	11·8	11·1	6·8	48·3	10·0	80·8
3·8	13·7	12·9	7·0	50·6	10·2	82·0
4·0	15·5	14·1	7·2	52·9	10·4	82·9
4·2	17·6	16·9	7·4	55·8	10·6	83·9
4·4	19·9	19·6	7·6	58·6	10·8	84·9
4·6	22·4		7·8	61·7	11·0	86·0
4·8	24·8		8·0	63·7	11·2	87·7
5·0	27·1		8·2	65·6	11·4	89·7
5·2	29·5		8·4	67·5	11·6	92·0
5·4	31·8		8·6	69·3	11·8	95·0
5·6	34·2		8·8	71·0	12·0	99·6

In the first part of the table the two values of x recorded have the significance indicated above. For *p*H values above 4·4 x_1 and x_2 have almost identical magnitude. The quantities x_1 are particularly useful in the determination of *p*H by the following method of matching the hydrogen ion activity of an unknown solution.

The electrochemical cell:

Pt electrode	buffer and quinhydrone	salt bridge	unknown soln. and quinhydrone	Pt electrode

is set up, and the buffer solution is titrated with sodium hydroxide until there is no potential difference between the electrodes. A simple pointer galvanometer may be employed to indicate the null-point and no potentiometer is therefore required. The *p*H is found from the amount of sodium hydroxide used to produce a balance point.

This modified buffer solution has been used by us for several years. We have found it of considerable value in the rapid preparation of solutions of definite *p*H. It has the merit that only one standard solution need be kept and that the results are trustworthy to within a small fraction of a *p*H unit.

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Colour Tests for Chlorine, Ozone and Hypochlorites with Methane Base

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MOST of the colour tests for ozone aim at its identification in the gaseous state. The tests here described are based on the reactions of ozone and chlorine in solution, which can be compared with the corresponding reactions of hypochlorites.

Arnold and Mentzel[1] studied various tests that had been proposed for ozone (metaphenylenediamine, guaiacum, thallous salts, etc.), and found that they were not distinctive. They recommended the use of an alcoholic solution of 4.4′-tetramethyl-diamino-diphenylmethane ("methane base" or "tetramethyl base"). Test-paper soaked in this solution gives a blue colour with chlorine or bromine gas and a violet colour with ozone. Their results were confirmed by Fischer and Marx.[2] Even this reagent, however, has certain limitations, as is shown below. The fluorescein test (Benoist[3]) is sensitive, but hypochlorites (at all events when impure) also discharge the colour and the fluorescence. In the present investigation the behaviour of methane base with liquids containing chlorine hypochlorite and ozone respectively has been studied.

METHANE BASE.—The base is readily soluble in carbon tetrachloride, but less soluble in alcohol or acetone. If ozone or chlorine gas is led into such solutions a range of colours is produced. The presence of an acid appears to be necessary for the colour reactions; acetic acid is usually added, but equally good reactions, although slightly differing in the shade of colour, can be obtained with hydrochloric or phosphoric acid. The same range of colours is produced by leading ozone through dilute alcoholic solutions or by exposing the solutions to ultra-violet rays; the concentration of the solution affects only the intensity of the colours.

First an indigo-violet colour is produced, which gradually deepens in intensity to purple-violet or amethyst, and then gradually changes to rose, and finally, after some time, to reddish-amber or ruby-red. These "ozone colours" are probably stages in the progressive oxidation of the methane base, and their gradual formation, after supply of ozone is discontinued at the violet stage, is characteristic.

If chlorine gas is led through any of the solutions of methane base a blue colour is produced. In a carbon tetrachloride solution acidified with glacial acetic acid the blue changes gradually to green and finally to yellow. If dilute acetic acid is used the same series of colours is produced, but is confined to the supernatant aqueous layer. In no instance was it possible to obtain with chlorine gas any of the above-mentioned series of "oxygen colours" produced by ozone.* If water is added to the alcoholic methane base solution, the chlorine colours are much intensified and an extended series is produced. The deep (Solway) blue first formed changes successively to grass-green, olive-green, orange and yellow, and finally the solution becomes colourless. As the colours pass from blue through grass-green a transient crimson colour can also be seen by transmitted light, but this disappears when the olive-green stage is reached.

The reactions of methane base with ozone and with chlorine in solution may, therefore, be summarised as follows:

	Ozone		Chlorine
1	Violet	1	Blue
2	Amethyst	2	Grass-green
3	Rose	3	Olive-green
4	Ruby-red	4	Orange
	—	5	Yellow

HYPOCHLORITES AS CHLORINATORS.—Various types of hypochlorites (see Table I) were used. From the analyses in the table it will be seen that in E the hypochlorite was in the form of hypochlorous acid and no sodium salts were present. F had a low alkalinity, whilst C and D were more alkaline than A and B.

TABLE I

ANALYSES OF TYPICAL HYPOCHLORITE SOLUTIONS†

(Each adjusted to contain 5 g. of available chlorine per litre)

	Sodium hypochlorite g. per litre	Sodium chlorate g. per litre	Sodium chloride g. per litre	Sodium oxide g. per litre
A ..	5·25	0·599	86·6	0·34
B ..	5·25	1·146	54·0	0·42
C ..	5·25	0·427	6·88	0·96
D ..	5·25	0·33	5·26	1·00
F ..	5·25	0·141	4·07	0·19

	Hypochlorous acid g. per litre	Calcium chlorate g. per litre	Calcium chloride g. per litre
E ..	3·71	0·71	7·7

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* Sometimes the chlorine yellow may assume an amber tint which is difficult to distinguish from the ruby-red "oxygen" colour.

† A, an electrolytic hypochlorite produced commercially in England; B, an electrolytic hypochlorite produced commercially in America; C, a chemically prepared hypochlorite, from bleaching powder and sodium carbonate; D, a similar product to which boric acid has been added (after Dakin); E, a solution of hypochlorous acid usually termed Eusol; F, a commercial hypochlorite, chemically prepared.

In aqueous solutions a hypochlorite produces with methane base a range of "chlorine" colours ending with complete bleaching. The following method of applying the test was finally adopted.

Three ml. of a 1 per cent. solution of methane base in 95 per cent. alcohol were placed in each of a series of test-tubes, and into each tube was introduced 40 ml. of dilute acetic acid (1·5 ml. of 5 *N* acid + 98·5 of water). Increasing doses of the hypochlorite (0·5 ml. to 10 ml. or more) were added to the acid reagent, and finally the contents of each tube were made up to 55 ml. with the dilute acid, well shaken, and left for several days. As a rule, when the hypochlorite was added prior to the dilution with the acid the colours were more brilliant. These colours are identical with those produced by chlorine gas and appear in the same order. Their formation depends strictly upon the relative quantity of hypochlorite to methane base, and by calculating a coefficient from $\frac{\text{mg. of methane base}}{\text{mg. of available Cl}}$, the following colour scale can be constructed:

6 to 1·5	Blue, increasing in intensity
1·5 „ 1·0	Blue-green to grass-green
1·0 „ 0·8	Olive-green to brown
0·8 „ 0·6	Orange
0·6 „ 0·5	Yellow
0·5 „ 0·3	Primrose-yellow
0·3 „ 0·0	Colourless

The figures do not appear to be affected by the use of hypochlorite or methane base of different concentrations. The colours are somewhat transitory, especially the greens, olive-green and orange, and the series thus eventually becomes one of blues and pale yellows with a greyish intermediary.

Tests were made at time intervals to ascertain if the change of colour is due to the further chlorinating action of available chlorine in the solution, and the following results were obtained*:

$\frac{\text{Methane base}}{\text{Available chlorine}}$	Immediate	1 hour	2 to 8 hours	24 hours
3·0	—			
2·0	—			
1·7	+			
1·5	+			
1·36	+			
1·20	+	+	+	—
1·10	+	+	+	—

In the immediate reaction available chlorine persisted in all the series except the two weakest.

After 1 hour all active chlorine was lost in the series down to 1·5, which covers all the blue colours. The transitory greens and oranges from 1·5 downwards are in a region where the chlorine persists for some hours, so that further changes in colour might be expected.

Titration of methane base against a hypochlorite (iodide and starch) shows that 2·5 mg. of the former are equivalent to 1 mg. of the latter. In any mixture in which the coefficient is less than 2·5/1, free active chlorine will be present. It appears therefore that the colours beyond blue (green, orange and yellow) are produced by further chlorination of the blue products first formed. It seems reasonable to assume that a blue and a yellow compound are formed and that other colours are produced by a mixture of the two.

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* + indicates the presence of available chlorine; — its absence.

At the end of 24 hours a period of comparative stability is reached (see Table II). All the series with a coefficient below 1·0 were completely bleached and those from 1·0 to 1·5 had lost their original tints of green and orange.

TABLE II

COLOUR REACTIONS OF CERTAIN HYPOCHLORITES WITH METHANE BASE IN AQUEOUS SOLUTION

(After 24 hours)

No.	Hypochlorite ml.	Available Cl mg.	E	F	D	A	B	A with added KOH
1	0·5	2·5	Light blue	Light blue	Blue	Pale blue	Pale blue	Pink
2	1·0	5·0	Blue	Blue	Light blue	Blue	Blue	Fawn
3	1·5	7·5	,,	,,	,, ,,	,,	,,	Beige
4	2·0	10·0	,,	,,	,, ,,	,,	,,	Pale brown
5	2·5	12·5	,,	,,	Very pale blue	Violet-blue	Violet-blue	Brown
6	3·0	15·0	Light blue	Light blue	Faint yellow	Violet-blue	Violet-blue	,,
7	3·5	17·5	,, ,,	Pale blue	Faint yellow	Blue-violet	Blue-violet*	,,
8	4·0	20·0	Very pale blue	,, ,,	Faint yellow	Violet	Violet	,,
9	4·5	22·5	Very pale blue	Faint yellow	Colourless	Amethyst	Amethyst	,,
10	5·0	25·0	Very pale blue	Faint yellow	,,	Rose	Rose*	,,
11	5·5	27·5	Colourless	Nearly colourless	,,	,,	,,	,,
12	6·0	30·0	,,	Colourless	,,	,,	,,	Orange

* The violet and rose are paler than in A.

The difference in the reaction of chemically and electrolytically prepared hypochlorites is very pronounced (see Table II); only after 4 or more days' standing can faint rose or violet tints be discerned in the former. When ozone was passed through the solutions of the electrolytic series (A and B, Table I) the earlier blues were unaffected, whilst the "oxygen" colours were intensified. Since the electrolytic products contained slightly more sodium chlorate and much more sodium chloride than the chemically prepared hypochlorites, samples of the latter were adjusted to contain the same amounts of chlorate and chloride as the former, and were then tested in the usual way. The addition of chlorate alone did not cause any material change except a tendency towards a slight brownish tint in two of the samples, but sodium chloride had an intensifying effect upon the colours; this was also noticeable with the colours produced by ozone gas, probably because ozone is more soluble in sodium chloride solution than in water.

The addition of a large excess of potassium hydroxide converts the colours into a series of secondary tints. Alkali, in the small degree in which it was present in the samples of hypochlorites tested, promotes bleaching, but does not affect the nature of the colours. In support of the view that the differences between the two classes of hypochlorites may be due to the presence of ozone in the electrolytic class, it may be pointed out that Schönbein (1840) demonstrated the presence of ozone in the gases evolved during the electrolysis of acidulated water and of salt solutions, and that Archibald and Wartenburg[4] showed that the solubility of ozone in neutral salt solutions is often greater than in water, and that such ozone solutions are more stable. Thus in the electrolysis of brine or magnesium chloride, conditions are present for the production and retention of ozone as well as of hypochlorites. It is suggested that, although chemically prepared hypochlorites may originally contain no ozone, yet ozone may be generated by secondary reactions and give the typical colour reactions. At all events, it is clear that some oxidising agent other than hypochlorite is present in electrolytic hypochlorites and is slowly developed in chemical hypochlorites. It is known that sodium hypochlorite decomposes, on standing, into chloride and chlorate, and according to Clarens,[5] a chlorite is produced as an intermediate product. Foerster and Dolch[6] found that at 50° C. hypochlorite is decomposed into chlorite and chloride, with liberation of oxygen, and that the chlorite is then converted into chlorate and chloride. According to Levi and Natta,[7] solutions of chlorites are not decomposed at 100° C. in the absence of a catalyst, even when hydrogen and oxygen are passed through them, but are decomposed in sunlight, with the production of ozone. Possibly, therefore, the colour reactions given by chemical hypochlorites with methane base may be due to the slow formation of chlorite, which then breaks up, yielding ozone as one of its decomposition products.

Allmand and Spinks[8] have shown that the action of light upon gaseous mixtures of chlorine and ozone results in the synthesis of ClO_3; under suitable conditions a reversal of this reaction might produce free ozone.

Hypochlorite solutions not only absorb ultra-violet rays, but, according to Mallet,[9] will emit them. It is therefore conceivable that the ultra-violet rays given off by the hypochlorite will gradually produce traces of ozone, which will react with methane base. With such an interpretation it is possible that the electrolytic hypochlorites differ from the "chemical" products in their more active production of ultra-violet rays, but the difference between the two classes is so marked that it seems more reasonable to assume that the electrolytic products contain ozone produced in the process of electrolysis.

TESTS WITH FLUORESCEIN.—Benoist[3] found that a solution of 1 part of fluorescein in a million is decolorised by a trace of ozone, and that 1 part in 10 millions loses its fluorescence but not its colour. On the other hand, chlorine, even when present in 3 times the amount of fluorescein, does not destroy even the fluorescence of a solution of 1 p.p.m. Egorov[10] also used a standard alkaline solution of fluorescein for the quantitative estimation of ozone, and the qualitative value of the test was confirmed by Allen.[11]

Standard aqueous solutions of fluorescein ranging from 1 to 10 p.p.m. were prepared. Five ml. of the hypochlorite solutions under examination were added to 10 ml. of the 10 p.p.m. solution, the mixture was allowed to stand, and the rates of bleaching were determined from time to time by comparison with the standards. The results (Table III) showed that the chemically prepared hypochlorites had much less effect than the electrolytic products on the fluorescein. For example, in one series of tests, whilst the solution containing sample A was completely bleached at the end of two hours, D was not completely decolorised even after 5 hours. Sample E (Table I), having an acid reaction, was instantly decolorised, so that it was not available for this test.

TABLE III

REACTION OF CERTAIN HYPOCHLORITES WITH FLUORESCEIN

(Degrees of colour)

		Parts of fluorescein per million									
		10	9	8	7	6	5	4	3	2	1
	Hours:	½	1	1½	2	2½	3	3½	4	4½	5
Samples	D	10	8	6	5/4	3/2	2/1	2/1	1	1/0	1/0
	F	10	7	6/5	5/4	3	2/1	2/1	1	1/0	0
	B	4/3	2	1	0	—	—	—	—	—	—
	A	3	2/1	1/0	0	—	—	—	—	—	—

The presence of ozone in the electrolytic hypochlorites would afford a reasonable explanation of these differences.

Samples of A and C were examined spectroscopically at the National Physical Laboratory. It was found that both were opaque to radiations of wave-length shorter than 0·4μ, and since the principal and most characteristic ozone bands are in the ultra-violet region in wave-lengths of less than 0·3μ, it was not possible by this means to detect ozone in the solutions.

HYPOCHLORITES AS OXIDISING AGENTS.—Since hypochlorites can act as either chlorinating or oxidising agents according to the particular substances, *e.g.* metals,

TABLE IV

COLOUR REACTIONS OF HYPOCHLORITES TO METHANE BASE IN PRESENCE OF EXCESS OF ALCOHOL

	Hypochlorite ml.	Methane base		
		10 ml.	3 ml.	1 ml.
1	0·5	Violet, amethyst rose, to ruby-red	Violet, amethyst rose, to ruby-red	Amber
2	1·0	„ „	„ „	Pale amber
3	1·5	„ „	„ „	Very pale amber
4	2·0	„ „	„ „	Colourless (clear)
5	2·5	„ „	„ „	„ „
6	3·0	„ „	„ „	„ „
7	3·5	„ „	Pale „ „	„ (cloudy)
8	4·0	„ „	Very pale yellow	„ „
9	4·5	„ „	„ „ „	„ „

on which they act, an attempt was made to reproduce the "oxygen" series of colours by using hypochlorite as an oxidising agent. It was found that when excess of ethyl alcohol is present, the "oxygen" colours are produced. A 1 per cent. alcoholic solution of methane base was treated with the hypochlorite solution (5 g. of available chlorine per litre), 0·1 ml. of 5 *N* acetic acid was added to each sample, and the mixture was made up to 55 ml. with alcohol. The results are shown in Table IV.

In every instance a blue colour was first formed, but disappeared on shaking, and then in the 10-ml. series a complete range of colours, corresponding exactly with that formed by ozone, was obtained (see Table V). In these tests no marked difference in the reactions were observed between the chemical and the electrolytic hypochlorites. The conditions under which hypochlorite acts as an oxidising agent towards methane base are: (1) the presence of excess of alcohol with a minimum quantity of water; (2) excess of methane base over hypochlorite.

TABLE V

COLOUR REACTIONS OF CERTAIN HYPOCHLORITES WITH METHANE BASE IN ALCOHOLIC AND AQUEOUS SOLUTIONS

(3·5 ml. of hypochlorite; 5 g. of available chlorine per litre; 3·0 ml. of 1 per cent. methane base solution + 0·1 ml. of 5 *N* acetic acid)

				Chemically prepared sodium hypochlorite		Electrolytically prepared sodium hypochlorite	
		Water	Alcohol	5 mins.	1 to 3 days	5 mins.	1 to 3 days
Cloudy	A	48	0	White	Pale blue	Blue	Blue
	B	44	4	,,	,, ,,	,,	,,
	C	40	8	Yellow	,, ,,	,,	,,
	D	36	12	Olive	Greenish blue	,,	,,
	E	32	16	Green	,, ,,	,,	,,
	F	28	20	Blue	,, ,,	,,	,,
	G	24	24	Indigo	Grey	,,	Violet
Clear	H	20	28	Violet	Yellow (br.)	Pale green	,,
	I	16	32	Amethyst	,, ,,	Violet	Amethyst
	J	12	36	,,	,, ,,	,,	,,
	K	8	40	Rose	,, ,,	Amethyst	Rose
	L	4	44	,,	,, ,,	Pale amethyst	Ruby-red
	M	0	48	,,	,, ,,	Rose	Pale ruby-red

If the proportion of the two reagents is kept constant but the proportions of water and alcohol varied (Table V), it is found that whilst the water is in excess a series of "chlorine" colours is produced. This is followed by a complete series of "oxygen" colours from violet to ruby as the amount of alcohol rises from 50 to 100 per cent. The water apparently throws the methane base out of solution and thereby reduces the proportion of this reagent to the hypochlorite.

Only when the proportion of alcohol exceeds 50 per cent. is all the methane base held in solution. Moreover, the reaction between alcohol and hypochlorite tends to reduce the quantity of the latter very rapidly. In the presence of methane base in addition, the destruction of available chlorine is still more rapid.

One minute after mixing the available chlorine can be traced in mixtures containing up to 50 per cent. of alcohol, but after five minutes there is an absence of available chlorine throughout the whole series, except the first two.

CONCLUSIONS.—(1) The addition of ozone gas to a solution of methane base gives a sequence of characteristic colours, namely, violet, amethyst, rose, and ruby red. The addition of chlorine gas to a solution of the base gives another sequence of characteristic colours, namely, blue, grass-green, olive-green, orange and yellow with final complete bleaching.

(2) Hypochlorites, in aqueous solution, give, in the first instance, the "chlorine" sequence of colours. They can also be made to give the "ozone" sequence, probably by direct oxidation, by concentrating the methane base in alcoholic solution.

(3) In aqueous solutions, electrolytically prepared hypochlorites give the sequence of "chlorine" colours with the base and also the complete sequence of "oxygen" colours, which become recognisable a few hours after the "chlorine" colours.

(4) Chemically prepared hypochlorites in the same solutions give no such "oxygen" colour reactions. After prolonged standing, these hypochlorites are capable of giving partial "oxygen" colours. These colours can in some degree be intensified and their production accelerated by addition of sodium chloride.

(5) Electrolytically prepared hypochlorites are capable of decolorising solutions of fluorescein much more rapidly than those prepared chemically.

(6) It is suggested that these important differences in colour reactions between the electrolytically and chemically prepared hypochlorites may be due to the presence of ozone in the former.

I desire to acknowledge the valuable assistance of Mr. E. A. R. Bousfield, B.Sc., A.I.C., in preparing and carrying out the extensive series of experiments herein detailed.

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MILTON PROPRIETARY LIMITED
10–12, BREWERY ROAD
LONDON, N.7

February, 1939

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE OCCURRENCE OF CYANOGENETIC SUBSTANCES IN EDIBLE MEMBERS OF THE CRUCIFERAE

INVESTIGATORS of cyanogenetic substances often entirely ignore the presence of these compounds in members of the *Cruciferae* that are used as human foodstuffs. In view of this I am anxious to record such literature as I have collected and such experiments as I have had time to perform.

The earliest reference is by Hoffman,[1] who by steam-distillation of cabbages and other members of the sub-family *Brassica* obtained oils which, on further fractionation, gave nitriles. Phenyl propionic nitrile was found in watercress and phenyl acetic nitrile in nasturtium.

Further observations were not made until 1928, when Chesney *et al.*[2] found that prolonged feeding of cabbage to rabbits produced goitre. This is not surprising, since a well-known method of biological standardisation of thyroid preparations is by feeding mice with aceto-nitrile and the thyroid preparation whose value is to be assessed.

Marine, Cipra and co-workers[3] ascribed the following properties to the goitrogenic principle. Prolonged steaming of cabbage may actually increase the goitrogenic properties; drying by air or *in vacuo* causes loss of the agent; alkaline hydrolysis extracts or destroys it, but acid hydrolysis is much milder in its effect. The active agent is soluble in ether and ethereal solvents, and its amount varies with seasonal and climatic changes. These properties are easily explained by the known chemical behaviour of nitriles.

Later[4] the same workers showed that cyanides are goitrogenic by depression of oxygen capacity, and also that methyl cyanide produces exophthalmic goitre.

Cyanides are used in the estimation of circulatory rate, since they depress the activity of the carotid body and hence affect the respiratory rhythm, and in an investigation it was found that the urine passed in 3½ hours by persons who had previously partaken of cabbage and brussels sprouts at the immediately previous meal, contained from 1·6 to 8·6 mg. of sodium cyanide.[5] Prior to the meal the urines were free from cyanide.

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THE BERNHARD BARON RESEARCH LABORATORIES
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May, 1939

A CHARACTERISTIC REACTION OF DITHIO-OXAMIDE WITH FERROUS IRON

DITHIO-OXAMIDE, rubeanic acid ($H_2N.CS.CS.NH_2$), is used as a very sensitive reagent for nickel, cobalt and copper (P. and R. M. Rây[1]). The reagent also gives reactions with a number of other metallic salts,[2,3,4] and with ferro-aquo ions ($(Fe(CN)_5H_2O)'''$) giving a blue colour.[5] With regard to its behaviour with iron salts, the relevant statements found in the literature are, that it does not give any precipitate with them,[6] and that iron does not interfere with the detection of copper or nickel.[7] On testing the behaviour of an alcoholic solution of dithio-oxamide with ferrous and ferric salts in neutral and acid solution, however, I obtained a reaction in which a dark precipitate, probably a ferrous salt of dithio-oxamide, was produced. This occurred when the reagent was mixed with a solution of ferrous salt (ferrous ammonium sulphate or ferrous chloride) containing sodium acetate. No further investigation of this reaction was made, because it did not seem to be distinctive. In alkaline solution, however, there was a distinct blue colour reaction, the characteristics of which were studied by three different methods:

(1) *Interaction of excess of cold alkaline solution of dithio-oxamide with a ferrous salt.*—When 1 or 2 drops of a 0·05 *M* neutral or slightly acid solution of ferrous salt were treated in a test-tube with 0·5 to 1 ml. of a freshly-prepared, cold alkaline solution of dithio-oxamide a deep blue colour, which changed on standing, was produced. The reaction was carried out with ferrous ammonium sulphate and with ferrous chloride, and the alkali used was sodium hydroxide in concentrations of 1·2 and 2·5 *N*. The concentration of the dithio-oxamide solution was 20 to 40 mg. in 20 ml. of alkali solution.

(2) *Interaction of excess of alkaline solution of dithio-oxamide with ferric salts in presence of a reducing agent.*—One or two ml. of an alkaline solution of dithio-oxamide (strength as above) were treated first with a little sodium hydrosulphite, $Na_2S_2O_4$, and then with 1 or 2 drops of a 0·01 *M* solution of a ferric salt (ferric ammonium sulphate or ferric chloride). The blue colour appeared immediately; even with a 0·001 *M* solution the reaction was distinct, though faint.

(3) *Solution of metallic iron in an alkaline solution of dithio-oxamide.*—It was found that metallic iron behaves in an interesting manner in an alkaline solution of dithio-oxamide. When a piece of electrolytic iron wire was left in the solution, the pale yellow colour showed very little, if any, change, even after 20 to 30 minutes; but immediately after the iron wire had been made cathodic for a few seconds in the solution against another iron wire as anode, or after it had been touched with a piece of zinc or aluminium wire, it began to dissolve, imparting an intensely blue colour to the liquid.

These facts seem to indicate that the colour is due to a reaction between bivalent iron and dithio-oxamide in alkaline solution. As found by P. and R. M. Rây,[1] nickel and cobalt also give *soluble* compounds with dithio-oxamide in presence of alkali. The blue ferrous compound, the colour of which is similar to that of the ferrous compounds of *iso*nitrosoketones, is not very stable. After some time it changes, probably owing to oxidation or decomposition.

GUSTAV NILSSON

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NOBEL INSTITUTE
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May, 1939

A SIMPLE MICRO-TEST FOR COPPER

DURING an investigation on the reduction of evaporation from water surfaces by uni- and multi-molecular surface films, it was found that a drop of oleic acid, placed on a water surface, assumed a blue-green colour when certain samples of distilled water, which had been kept in a copper container, were used. A micro-test using sodium diethyl-dithiocarbamate,[1] revealed that the copper concentration was of the order of 5 in 10^5. On pursuing the matter further, it became evident that the blue coloration of oleic acid, which is due to the formation of copper oleate, may be used as a test for small amounts of copper. The colour is almost a pure blue when pure oleic acid is employed; with commercial samples of oleic acid the colour is blue-green or green owing to the yellow colour of the acid.

The test is almost as sensitive as that with sodium diethyldithiocarbamate, as is shown in Table I.

TABLE I

Concentration of copper	Oleic acid (0·05 ml. on 100 ml. of soln.)	Diethyl-dithiocarbamate
1 part in 10^4	Deep blue-green (green solid deposit after 1 day)	—
1 ,, ,, 10^5	Less deeply coloured	Turbid brown (prec.)
1 ,, ,, 10^6	Pale blue-green	Brownish-yellow
5 ,, ,, 10^7	Very pale	Pale lemon yellow
1 ,, ,, 10^7	No colour	Hardly perceptible yellow

Table I shows that a concentration of copper as low as 0·5 to 1 part in 10^6 can be detected when 100 ml. of solution and a drop of oleic acid of about 0·05 ml. are used. The sensitivity may be further increased by employing a larger volume of solution, since the method is virtually a concentration, in a small drop of oleic acid, of a large fraction of the copper present. In an experiment in which 1 litre of solution was used, the pale green colour was detected when the concentration of copper was only 1 in 10^7.

The *p*H of the solution should be between 5 and 8 (Table II). Within this range the intensity of the colour is practically independent of the *p*H. At *p*H values lower than 3 to 4 and higher than 9 to 10 no colour is observed. Copper oleate is obviously not very stable in presence of acid; on the other hand, in alkaline solutions the concentration of Cu^{++} is very small, owing to the formation of hydroxide. It is seen from Table II that the optimum range is between 5 and 7.

TABLE II

Concentration of copper	Colours at varying *p*H 3	4·3	5	6–7	8	10
1 part in 10^4	Nil	Deep blue-green		Deep blue-green		
1 ,, ,, 10^6	Nil	Nil	Pale green	Pale blue-green		Faint blue

When the drop of oleic acid is placed on the solution and the system is merely allowed to stand, the colour may take one day to develop. The time is considerably shortened, however, by stirring the solution continuously or simply by boiling. With a solution containing 1 part of copper in 10^6 the maximum colour appeared after 20 minutes on stirring and after 5 minutes on boiling (Table III).

It is advisable to stir the solution in such a way that no appreciable emulsification takes place, since the droplets may not unite readily after agitation has ceased. For this reason shaking is not advisable.

The test is not seriously affected by other metals which may be present in the solution. Cobalt, nickel and chromium do not produce any colour with oleic acid, nor does manganese unless present in very large amounts. Ferric salts cause a reddish-brown coloration of the oleic acid due to the formation of ferric oleate. If the iron concentration is less than about 1 part in 10^4 no precautions need be taken, since the colour due to the iron is then only yellow, which turns the copper colour to green-yellow. If iron is present in larger quantities, its colour will interfere with the colour produced by the copper. In that event tartaric acid neutralised with sodium hydroxide should be added. To 100 ml. of $N/100$ ferric chloride solution, which contained tartaric acid that had been neutralised with sodium hydroxide (litmus), 1 ml. of water containing 1 part of copper in 10^4 was added, so that the end-concentration of copper was 1 in 10^6. With this solution the oleic acid test was carried out. The drop showed a definite pale blue-green colour which was easily visible above the yellow complex ferric salt solution.

TABLE III

0·05 ml. of oleic acid on 100 ml. of solution

Concentration of copper	Time of maximum colour on Standing	Stirring	Boiling
1 part in 10^4	18 hours	20 mins.	Colour appears almost immediately
1 ,, ,, 10^5	18 ,,	20 ,,	
1 ,, ,, 10^6	2 days	20 ,,	5 mins.
5 parts in 10^7		½ to 1 hour	

Marcille[2] reports that the green colour occasionally exhibited by olive oils is due to a compound of copper with chlorophyll, which is sometimes present in the olive oil. Another possibility is that the colour is due to the formation of copper oleate. A drop of triolein placed on water which contained 5 parts of copper in 10^5, developed a green colour, obviously due to a certain amount of hydrolysis of the triolein.

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CHEMISTRY DEPARTMENT
UNIVERSITY OF MELBOURNE

Official Appointment

THE Minister of Health has approved the following appointment:

DONALD CLARENCE GARRATT as Public Analyst for the Metropolitan Borough of Camberwell, in place of Martin Priest (retired).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

ROYAL BOROUGH OF KENSINGTON

REPORT OF THE PUBLIC ANALYST FOR THE FOURTH QUARTER, 1938

OF the 332 samples of food and drugs examined, 216 were purchased formally.

HAIR LOTION CONTAINING CARBON TETRACHLORIDE.—A bottle of hair lotion was submitted for analysis with the information that it had caused unconsciousness in a woman who had used it. It was found to consist essentially of a mixture of paraffin hydrocarbons with carbon tetrachloride. As the public cannot be expected to be aware of the anaesthetic and toxic properties of carbon tetrachloride, it seems desirable either that its sale in shampoos and preparations of a similar nature should be prohibited, or that it should be permitted only when labelled with a caution as to its dangers.

F. W. EDWARDS

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

PROCESSED CHEESE

IN September of last year a firm was prosecuted and convicted at Slough for selling as "Finest Cheddar" a processed cheese which had been made from partly skimmed milk instead of from whole milk as is customary with hard cheeses of the Cheddar type. Since then the question of the composition of processed cheese has been taken further by a request from this Society to the Ministry of Health that a limit of water be fixed at a maximum of 42 per cent., with a minimum fat-content of 45 per cent. calculated on the dry matter.

The water-content of processed cheese has, in recent years, steadily increased and is still increasing, and, in an endeavour to put some check on the practice, a firm of processed cheese manufacturers was summoned, on May 26th, at Slough, under Section 30 of the Food and Drugs (Adulteration) Act, for selling cheese falsely labelled as "Gruyère" and "Packet Cheddar." The purchased sample, which bore the label "Gruyère," was found to contain 49·01 per cent. of water, and that labelled "Packet Cheddar," 48·27 per cent. of water. The prosecution maintained that, whilst Gruyère and Cheddar were essentially whole-milk cheeses containing, before processing, about 35 per cent. of water, there was no requirement in the process of manufacture that afforded any justification for the addition of such large extra quantities of water in making a satisfactory processed cheese. Evidence in support of this view was given by Mr. Eric Voelcker, F.I.C., the County Analyst, and by Dr. H. E. Cox, F.I.C. The amounts of water found were considered to be excessive and to correspond to the adulteration, with water, of milk, whiskey, or other food or drink. Since notice of the adulteration was not given, it was considered to be a fraud on the public.

For the defence Dr. E. J. Parry, F.I.C., contended that it was impossible to prepare cheese for packing in small sections without adding water, and he considered that the labels correctly described the cheeses.

The firm was convicted and fined £10 with 10 guineas costs. The Bench, when asked to fix a standard of water-content of packet cheese which could bear these labels, decided that 40 per cent. was a very fair standard.

It was stated in court that no further proceedings would be taken, up to September 30th, on stocks already sold to shops prior to the cases just heard.

There have recently been three further prosecutions. In the first of these a firm was fined £2 2s. 0d., with £6 6s. 0d. costs, at Henley-on-Thames, Oxfordshire, for selling Cheddar cheese containing 50·25 per cent. of water. The bench were not prepared to make any standard for water in cheese, but were willing to accept that laid down by the Slough magistrates. In the second case, also tried at Henley, on June 16th, a fine of £5, with £6 6s. 0d. costs, was imposed for the sale of Cheddar cheese containing 48·51 per cent. of water. The defendants in the third case pleaded guilty to selling "Finest Cheddar" cheese containing 51·44 per cent. of water, and on June 23rd were fined £10 0s. 0d., with £7 0s. 6d. costs, at Ivinghoe, Buckinghamshire.

Ministry of Health

THE BACTERIOLOGICAL EXAMINATION OF WATER SUPPLIES

The first report on this subject was published by the Ministry of Health in 1934 and reprinted in 1936. It has been revised and extensively re-written by an Office Committee, the names of the members of which are given below.† The Report is divided into two parts—General and Technical—and contains four appendixes, dealing with (A) Sampling, (B) Apparatus, (C) Media, and (D) Probability Tables.

Part I, General (pages 1–17) is divided into seven sections under the following headings: (I) Introduction, (II) Taking of Samples, (III) The Rationale of the Bacteriological Analysis of Water, (IV) Frequency and Type of Examination, (V) Interpretation of Results, and (VI) Suggested Classification of Waters.

Part II, Technical (pages 18–43), is divided into five sections: (VII) The Plate Count, (VIII) The Presumptive Coliform Count, (IX) The Differential Coliform Test, (X) The Faecal Streptococci Test, and (XI) The Clostridium Welchii Test.

The first part, although addressed to the non-technical reader, will be found of value by medical officers of health, water engineers and sanitary inspectors. It includes a simple description of the rationale of bacteriological examinations, considers the frequency and type of the examinations necessary, discusses at some length the interpretation of results, suggests a classification of piped water supplies into classes described as Highly Satisfactory, Satisfactory, Suspicious and Unsatisfactory, and gives appropriate standards for small rural supplies such as shallow wells, based on the Presumptive Coliform Count. Attention is drawn to the advantage of examining a number of samples by a simple test rather than occasional samples by more complicated tests, and it is suggested that a simple

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[*] Reports on Public Health and Medical Subjects, No. 71 (Revised Edition). H.M. Stationery Office, 1939. Price 1s. net.

[†] Ministry of Health Memo. No. 221. T. Carnwath, D.S.O., D.Sc., M.B., D.P.H. (Ministry of Health) (Chairman); J. F. Beale, M.A., M.R.C.S., L.R.C.P., D.P.H. (Counties Public Health Laboratories); D. B. Byles, B.Sc., F.I.C. (Deputy Director of Water Examination, Metropolitan Water Board); H. T. Calvert, M.B.E., D.Sc., F.I.C.; W. M. Scott, M.D., B.Sc., D.T.M. & Hy., and E. L. Sturdee, O.B.E., M.R.C.S., L.R.C.P., D.P.H. (Ministry of Health); E. W. Taylor, M.A., M.D., D.P.H. (Senior and Research Bacteriological Assistant, Metropolitan Water Board); Professor G. S. Wilson, M.D., F.R.C.P., D.P.H. (Professor of Bacteriology, London School of Hygiene and Tropical Medicine).

Coliform examination should be carried out daily by the larger water undertakings, and as frequently as possible by the smaller ones; at the same time the lesser importance of very frequent examination for upland surface supplies derived from moorland where there is little possibility of human contamination is admitted, and the greater importance of frequent examinations of water from deep wells sunk in fissured strata is emphasised.

In the second part of the Report the technique of the Coliform Count is dealt with at some length as being of major importance. What is known as the sampling error of the liquid dilution method (*i.e.* the error due to the chances of catching or missing a single bacterium in the particular quantity of sample taken for cultivation from the critical dilution) is considered, and the best way of eliminating this element of chance is described. This is effected by taking several equal portions and calculating the numbers present from tables compiled from the laws of probability by McCrady and modified by Swaroop. Such tables are given in an Appendix.

Four methods for the differentiation of coliform bacilli are given. In the first method (A) primary cultures are made in MacConkey's broth at 37° C., and plated out on bile salt agar after 24 hours, and colonies are selected for the M.R., V.P., citrate, indole and gelatin-liquefaction tests. In the second method (B) the cultures in MacConkey's broth are incubated at 37° C., and those showing gas formation are subcultured in MacConkey's broth at 44° C. Gas formation at the latter temperature indicates Type I or Type II (faecal) *B. coli.* If no gas is shown at 44° C., the tubes showing gas at 37° C. are subcultured in Koser's citrate broth and incubated at 37° C.; growth in 2 to 3 days is regarded as presumptive evidence of organisms of the Intermediate-Aerogenes-Cloacae type. In the third method (B_2) the procedure is the same as in method (B_1), but if the MacConkey tubes incubated at 44° C. show no gas, those incubated at 37° C. are plated out, and colonies are selected and identified. In the fourth method (B_3) the primary cultures in MacConkey's broth are incubated at 44° C. Acid and gas production indicates faecal *B. coli*, and no account is taken of the other types. It is possible that the faecal *B. coli* content may be slightly underestimated by this method. The importance of maintaining the temperature strictly at 44° C. is emphasised. It is suggested that the simpler means of differentiation should be given a trial.

D. R. W.

Department of Scientific and Industrial Research

WATER POLLUTION RESEARCH BOARD

REPORT FOR THE YEAR ENDED JUNE 30TH, 1938

THIS, the Eleventh Annual Report of the Board, includes the Report of the Director (Dr. H. T. Calvert). The Report once more emphasises the necessity for constant vigilance on the part of those responsible for the supply of water to the public. The serious outbreak of typhoid fever at Croydon which, it is pointed out, was due to the infection of part of the public water supply of the district, focussed public attention on the importance of taking all practicable steps to protect sources of water from pollution, of systematic treatment of all supplies in any way liable to pollution, and of frequent examination of samples to ensure that the treatment is adequate. The Board say that any neglect of the lessons to be learnt from the Croydon outbreak would be deplorable. The research undertaken under the supervision of the Board includes investigations on the treatment of water for public supply and for industrial purposes, the treatment and disposal of domestic sewage and industrial effluents, and problems of pollution of rivers.

TREATMENT OF WATER WITH SYNTHETIC RESINS.—The discovery (*cf.* ANALYST, **1936, 61, 33; 1937, 62, 302; 1938, 63, 430**) in the course of the Board's work that acids, bases and salts can be removed from solution in water by means of certain synthetic resins has aroused widespread interest, both in this country and abroad, and considerable progress has been made in the development of the resins for industrial purposes by commercial firms who have acquired licenses for their manufacture and sale. The main applications of the resins up to the present have included the treatment of water to remove all or part of the dissolved salts; this had previously been possible only by more expensive methods, such as distillation. Utilisation of the resins for the removal of valuable substances, such as metals, from very dilute solutions (for example, from industrial effluents), and for the removal of objectionable substances in very low concentration in water is also being developed rapidly. Recent work under the Board has shown that, under certain conditions, fluorides, which are sometimes present in water in low concentrations, may be removed by *m*-phenylenediamine resin; the fluorine is not readily removed, however, when other salts usually found in natural waters are present. An important point in connection with the use of these resins for the treatment of drinking water is that, when freshly prepared, they contain some organic matter which is soluble in water. This soluble matter can, however, be removed from some of the resins by extraction several times with hot water.

LEAD IN DRINKING WATER.—The investigation to determine the average quantity of lead taken up by certain types of water from lead pipes and fittings under conditions of household supply has been continued, and tests have now been made on seventeen services in different parts of England and Scotland. The extent to which the water is contaminated by passage through lead pipes depends on the character of the water, the length and arrangement of the pipes, the rate of flow of water and other conditions. In consequence, large differences may occur from time to time in the concentration of lead in water withdrawn from any one service. In one of the tests, extending over several weeks, the average concentration of lead in the water was as high as 0·5 part per million; this concentration is too high if risk of lead poisoning is to be avoided. Experiments are in progress on methods of treatment of waters with the object of reducing their action on mains and service pipes of different materials. These methods, in general, aim at reducing the acidity or increasing the alkalinity of the water. At some works alkalis, such as lime, soda and calcium carbonate are added, in controlled quantities, to the water; at other works the water is passed through filters containing pieces of limestone, marble or magnesite (*cf.* ANALYST, **1938, 63, 302**).

STERILISATION OF SLOW SAND FILTERS.—For many years at a water works in Scotland slow sand filters had been used, and the filtered water had been of high quality. After the periods of drought in 1933 and 1934 an additional storage reservoir was brought into service, and six weeks later *B. coli* were found in 1 ml. of the filtered water. The primary and secondary slow sand filters were then sterilised with sodium hypochlorite, and within six days the high quality of the filtered water was regained, no *B. coli* being found in 100 ml. The method of treatment is outlined.

MILK FACTORY EFFLUENTS.—One of the most important of the Board's investigations is the work which is being carried out, in collaboration with the milk industry, on the treatment and disposal of waste waters from dairies and milk products factories. These waste waters have in the past caused serious pollution of streams into which they have been discharged. In 1935, after preliminary laboratory experiments, the Board erected two large-scale experimental plants at a milk-collecting and distributing depot and cheese factory at Ellesmere, Shropshire. Previous Annual Reports (*cf.* ANALYST, **1937, 62, 431; 1938, 63, 302**) have described the treatment of milk washings from the milk depot. It was shown that these liquids, which are difficult to treat by the method of biological filtration as ordinarily applied at sewage disposal works, could be satisfactorily purified when passed at a controlled rate through two percolating filters in series; the order in series is reversed periodically in order to prevent the accumulation of excessive amounts of solid matter in the filters. During the past year the waste waters treated have contained whey washings, which are produced during the manufacture of cheese. These washings are rather more difficult to purify than milk washings, but effluents of excellent quality have been obtained. With two percolating filters in series, the quantity of polluting matter which can be treated daily in filters of a given size is considerably greater than is usual in the treatment of sewage at a sewage disposal works, where the liquid is passed through only one filter. The new method has been adopted and is in satisfactory operation at a number of milk depots and cheese and butter factories. During the period 1935 to 1938 the industry contributed approximately £10,000 towards the cost of the investigation.

TREATMENT OF TOWN SEWAGE.—The new method of operating percolating filters has also aroused great interest among those concerned with the treatment and disposal of town sewage. The Birmingham, Tame and Rea District Drainage Board, which uses filters of a capital cost of nearly £1,000,000, has placed a new laboratory and suitable large-scale plant at the disposal of the Board in order that treatment of sewage by the new method may be tried on a large scale. The whole of the cost of the new laboratory and of necessary additions and modifications to the plant has been met by the Drainage Board.

ACTIVATED SLUDGE PROCESS OF SEWAGE TREATMENT.—The investigation, under the direction of Professor J. C. Drummond, has been continued (*cf.* ANALYST, 1937, **62**, 432). The results of experiments, described in detail, indicate that the disappearance of nitrite during the aeration of unsterilised mixtures of sewage and activated sludge is due to biological activity and not to simple chemical decomposition.

COLLOIDS IN SEWAGE.—Further work, under the supervision of Professor F. G. Donnan (*cf.* ANALYST, 1937, **62**, 432), has shown that change in the area of the surface of the bubbles, when gases were passed through sewage and through mixtures of sewage and activated sludge under the conditions of the experiments, had no appreciable effect on the amount of organic matter flocculated. Temperature has been found to have a pronounced influence on the coagulation, during aeration, of organic matter in mixtures of sewage and activated sludge. Aeration of sewage treated with synthetic resin (*m*-phenylenediamine resin) caused a comparatively rapid removal of organic carbon from the supernatant liquid, but the addition of this resin had no marked effect on the rate of removal of total nitrogen. On the other hand, the addition of sulphited quebracho tannin resin increased the amount of total nitrogen removed from sewage by aeration and centrifuging, but retarded the rate of removal of organic carbon; there was in fact an initial rise in the concentration of organic carbon. The results of experiments on the effect of proteins and various organic materials, together with sodium chloride, on the rate of sedimentation of quartz particles at various *p*H values are also described in detail.

RIVER MERSEY INVESTIGATION.—The investigation on the River Mersey, which was begun in 1933 and occupied about 4 years, has been completed and a comprehensive special report has been published as Water Pollution Research Technical Paper No. 7. A full summary of the experiments, observations and conclusions is included in the present Report. The work was undertaken at the request of the Merseyside Local Authorities, the Mersey Docks and Harbour Board, and other local interests, who agreed to meet the whole of the cost. Its object was to determine the effect of the discharge of crude sewage into the Estuary on the amount and hardness of the estuarine deposits. This problem, which was obviously one of considerable importance to the authorities responsible for the conservancy of the river and for the disposal of sewage of the Merseyside towns, had for many years been the subject of much local controversy. The investigation, which cost about £26,000, has been eminently successful in that it has given a definite answer to the difficult question asked in the terms of reference. It has led to the conclusion that the crude sewage discharged into the Estuary of the River Mersey has no appreciable effect on the amount and hardness of the deposits in the Estuary.

ATMOSPHERIC POLLUTION

Nineteen representatives of local authorities and other organisations co-operating with the Department of Scientific and Industrial Research in investigations into the nature and extent of atmospheric pollution met on June 6th in half-yearly conference at the offices of the Department. The gathering included representatives from Birmingham, Cardiff, Dagenham, Glasgow, Halifax, Leeds, Liverpool, London County Council, Manchester, Newcastle, Rotherham, Sheffield, Scunthorpe, Stoke-on-Trent, Willesden, Leicester, British Commercial Gas Association, and British Electrical Development Association.

Alderman D. Adams, M.P., J.P., of Newcastle, presided, and, at the close of the meeting, was unanimously re-elected Chairman of the Conference for a third year.

The Conference learned with interest of measurements which had been made in Scunthorpe by Dr. W. H. Hartston (the Medical Officer of Health), on the amounts of zinc and lead in the matter deposited from the air. Other members of the Conference who had had previous experience of measurements of zinc, lead and other metals in the atmosphere of steel-manufacturing and other towns, also took part in the discussion.

The Conference expressed its satisfaction at the welcome which had been given to the Public Health (Coal Mine Refuse) Bill in its recent passage through the House of Commons.

Dr. G. M. B. Dobson, F.R.S. (Chairman of the Atmospheric Pollution Research Committee) presented a report on the progress of the investigations carried out under the Committee. He told the Conference that the special survey of atmospheric pollution in and around the City of Leicester had now entered upon its third year, during which special attention would be paid to certain problems which the previous work of the survey had shown to be important. This had required the establishment of three new observing stations, for the measurement of dust in the air, near the city. Special work on these problems would also be carried on in the Laboratory during the year.

Royal Agricultural Society of England

ANNUAL REPORT OF THE CONSULTING CHEMIST

THE Report of the Consulting Chemist (Mr. Eric Voelcker, F.I.C.) gives *inter alia* particulars of matters of interest arising out of work done in the Society's Laboratory during the year. A striking feature was the number (43 out of a total of 127) of samples of water sent for analysis. This is a large increase and may have been due to the recent water scare, but several samples were went by members proposing to purchase new property.

HOUSEHOLD REFUSE AS SOURCE OF HUMUS.—This material is prepared from household refuse from which the bulk of the cinder and clinker has been removed by screening, after which the glass, tin, crockery, rags and some of the paper are picked out by hand. The particles of these that get past the pickers will be very small and not of any consequence. So far as possible the product, which is non-odorous, consists of the organic matter in the original refuse. Preliminary results of field trials indicate that it is of about the same value as dung, and with the increasing difficulty of obtaining sufficient farmyard manure, it may become of great importance not only to farming, but also to market garden production and horticulture.

Composition of "Horse Gram."—This is an Indian legume (*Dolichos biflorus*) which is largely used in India as cattle food, and the crop is grown both for fodder and for the seed. A sample gave the following analytical results:—Moisture, 9·57; oil, 0·43; albuminoids 22·87; carbohydrates, etc., 58·63; woody fibre, 4·93; mineral matter (ash), 3·57 per cent. The nitrogen-content was 3·66 per cent., and the ash included 0·60 per cent. of sand and silica. This material is quite distinct from the common gram or chick pea (*Cicer arietinum*). At times it has been imported into this country, but apparently not of recent years. It was found free from cyanogenetic glycosides and would appear to be a suitable seed for grinding and adding to animal foods. If it could be delivered here at a cheaper rate than peas or beans it would be worth a trial, but not otherwise.

Government of India

REPORT ON THE CHEMICAL LABORATORIES MAINTAINED BY THE CENTRAL BOARD OF REVENUE FOR 1937-38*

THE Control Laboratory (under the direction of the Special Chemical Adviser, Dr. H. B. Dunnicliff) remains in the Chemistry Department of the Government College, Lahore, but the plans and estimates for the building and equipment of the Control Laboratory at New Delhi have been finally approved. The laboratories of the Board render services to other Departments of the Government of India. Thus, all the Customs laboratories have been supplied with the standard apparatus for testing petroleum, and arrangements have been made whereby imported explosives shall be tested in those laboratories.

CLASSIFICATION OF SPIRITUOUS, MEDICINAL AND TOILET PREPARATIONS.—At the Excise Conference, held at Delhi in November, 1937, the question of the uniformity in rate of duty on spirituous medicinal and toilet preparations was discussed, and it was found necessary to divide them into three classes: (1) medicinal preparations of undeniable therapeutic value; (ii) preparations which, although commonly used in dispensing, were more of the nature of flavouring agents than medicines (*e.g.* Sir. Aurantii), or which could be used as beverages (*e.g.* tonic or medicated wines); (iii) toilet preparations and perfumery. It was decided that lists of preparations falling in class (ii) should be prepared by a technical co-ordinating officer appointed for all the Provincial Governments, and that this officer might most appropriately be under the control of the Central Board of Revenue.

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* Published by the Manager of Publications, Government of India Press, New Delhi, 1939. Price 1s. 3d.

INTERPRETATION OF THE TERM "DYEING."—The exact meaning of the terms "dyes" and "dyeing process" has again assumed some importance. The Board ordered that the term "dyeing" should be interpreted to mean the imparting of colour to textiles, leather, paper, fur and similar articles. The new definition necessitated the revision of the "Standard List of Tested Dyes" issued by the co-ordinating officer, the Chemical Examiner, Bombay Custom House. It was formerly the practice to consider coal-tar colours used in varnishes, soaps, etc., also as dyes under Sec. 30(1) of the Indian Customs Tariff.

DEFINITION OF GREASE.—The Board held that, for purposes of assessment, the term "grease" should be deemed to refer to substances which are solid at ordinary temperature. In cases of doubt the question whether an article should be classified as a "grease" or an "oil" should depend on the result of the "pour-point" test, whether or not the preparation contained soap.

Proposals on what should be considered as "lubricating greases," as distinguished from lubricating oils as specified in the Tariff, and in which cases and to what extent laboratory tests should be made have been adopted for circulation to the ports for opinion.

MORPHINE-CONTENT OF OPIUM.—The questions of the maximum morphine-content of Indian opium and the loss of morphine from opium on storage are receiving attention. The highest morphine strengths recorded in samples of opium collected from first lancings were as follows:

Opium from	Morphine, by B.P. method Per Cent.
Ghazipur	18·3
Gorakhpur	18·1
Gonda	17·2
Bareilly	16·8
Shahjehanpur	17·0

The remnants of these samples have been sealed in bottles for examination after some time, to ascertain if any fall in morphine strength occurs.

DEGRADATION OF OPIUM.—The degradation of opium in Malkhana vats, first observed in 1935, has caused some anxiety, and a systematic investigation to discover the cause and prevention of the trouble is in progress. In particular, an attempt is being made to determine if pasewa associated with opium during the time of collection has any connection with this deterioration. Although the existence of pasewa has been known for more than sixty years (see John Scott, *Report on the Experimental Cultivation of Opium Poppy*, Season 1876–77), this important subject has never been properly studied. The exact nature of pasewa is unknown, and no recent work has been done on its development or composition, with the exception that volatile aliphatic acids, especially acetic acid, have been detected in it. Preliminary work on cultivators' samples of doubtful origin has been begun, and a full investigation will be undertaken when authenticated samples collected at the time of the next opium collection (1939) have been received from the Opium Agent.

Ceylon

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1938

THE Government Analysts' Department (under the direction of Mr. J. V. Collins) now includes 5 chemists and 2 probationers, all of whom are qualified to sign reports and accept responsibility for their work. Prior to 1938, reports were signed only by the two senior members of the staff, who had thus to accept responsibility for analyses not actually made by them—obviously an improper arrangement if any of the reports had to be defended in court.

The amount of work submitted to the Department continues to increase. In 1938, 4095 articles were examined as compared with 3684 in 1937. In the 6 years since 1933 the number of reports issued has almost doubled. A similar increase has occurred in the number of criminal cases requiring investigation. The policy of sending police officers to be trained at the Police College, Hendon, and the detective classes held in Ceylon, are responsible for a considerable proportion of this increase. It is gratifying to record that "clues" were given to the police in a number of cases in which the Department was consulted.

POISONING CASES.—The number of cases investigated has remained remarkably constant from year to year, varying only from 88 to 95 in the past five years. In 42 of the 90 cases submitted in 1938 poison was detected. The poisons included arsenic, 10; potassium cyanide or prussic acid, 9; mercury, 4; strychnine, 4; acetic acid, sulphuric acid and croton oil, 3 each; copper salts, alcohol, quinine salts and powdered glass, 2 each. The remainder included a mydriatic alkaloid, nitric acid, potassium permanganate, salicylic acid, yellow phosphorus, *Petchia zeylanica* and an unidentified aromatic oil. In a case of abortion a hollow stalk, which contained a paste of arsenic and copper sulphate and smelt strongly of asafoetida, was used. The cases in which quinine was found were also concerned with abortion.

Identification of Glass.—In one of the poisoning cases in which powdered glass had been used it was possible to show that the particles separated from a curry had the same specific gravity as glass from the suspected source.

The method of determining the specific gravity of fragments of glass by immersion in a liquid the gravity of which can be varied at will has proved very useful. In a case in which a car had driven off after a fatal accident fragments of glass found at the scene corresponded with the glass of the broken headlights.

In another case it was possible to fit together a number of small fragments of glass found at the scene of a gang robbery, and to show that they formed part of the broken glass of a torch in the possession of one of the accused.

SHOOTING CASES.—The number of exhibits (173) examined in connection with 54 cases showed a very large increase over former years. In many cases it was possible to demonstrate that a cartridge had been fired from a gun produced. It was also possible to exclude a number of guns. By arrangement with the Customs the Department is informed whenever a new brand of cartridge is imported, and the reference collection thus formed has proved its value during the year.

EXPLOSIVES AND FIREWORKS.—Fifty-six samples of crackers and 114 of explosive mixtures and fireworks were analysed, and some of these were as dangerous as hand-grenades. Aluminium powder has a large and legitimate use in pyrotechnics for the production of golden rain, but in the locally manufactured fireworks its sole use is to produce a high explosive (*cf.* ANALYST, 1938, **63**, 502). Arsenic sulphide in conjunction with chlorate and sulphur is another popular, though prohibited, mixture. The state of the car of the Magistrate of Colombo, after a bomb filled with this explosive had been thrown at him, provides ample justification of this prohibition. The magistrate probably owes his life to the indifferent aim of his assailant.

The Mechanical Testing of Bituminous Road Materials*

THE Road (Materials and Construction) Research Board is appointed by the Department of Scientific and Industrial Research to advise generally on the conduct of research on road materials. The Ministry of Transport is similarly responsible for full-scale road experiments. A necessary preliminary to the study of the physical and mechanical properties of bituminous surfacings was obviously an examination of the literature, and a critical digest of this is given in the present Report.

The Introduction deals with the classification of bituminous road materials, their characteristic properties, the purpose of mechanical tests, and the classification of mechanical tests.

Part II discusses the principal mechanical tests under the following heads: (i) Tests involving plastic properties of the materials. (ii) Tests involving elastic properties of the materials. (iii) Miscellaneous tests. (iv) Service tests.

Part III, on Mechanical Tests and Road Practice, includes (i) Employment of mechanical tests in mixture design. (ii) Mechanical tests and the macadam types of surfacing.

Part IV contains a critical study of mechanical tests and discusses the influence of test conditions on the results obtained. It includes: (i) Effect of degree of compaction of the specimen. (ii) Effect of size of specimen. (iii) Effect of rate of loading. (iv) Effect of ageing of specimens. (v) Effect of temperature of test. (vi) Degree of reproducibility of results.

The following classification has been adopted in order to give some idea of current practice in bituminous road construction. Four main divisions may be distinguished according to the grading of the mineral matter, *viz.*

I. Tar or bituminous macadams, containing large aggregate only.
II. Mixtures containing a preponderance of large aggregate.
III. Mixtures containing a preponderance of fine material.
IV. Mixtures containing fine material only.

In practice the various groups suggested by these divisions tend to merge into each other, but the divisions are of assistance in indicating the broad outlines of current practice. The Report gives brief descriptions of the various types of construction falling into each main division.

The various papers discussed are tabulated in an alphabetical list of references, which contains 137 descriptive entries.

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* Road Research and Experiment. Special Report No. 1. A Survey of the Literature. By T. Lonsdale, M.Sc., Ph.D., F.Inst.P. Department of Scientific and Industrial Research and Ministry of Transport. Pp. 47. H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 1s. net.

Nomenclature of Hormones*

At the Third International Conference on the Standardisation of Hormones, held at Geneva, August 11th to 13th, 1938, the question of nomenclature was considered, and it was agreed:

(1) That the fully descriptive term "anterior lobe of the pituitary gland" should be adopted for reference to the organ in question in the records of the Conference.

No general agreement was reached in the discussion of the respective claims of the suffixes "trophic" and "tropic" in the construction of descriptive terms for reference to the active principles with which the Conference had dealt.

It was agreed:

(2) That the use of the forms with the suffix "trophic" or "tropic" in the official English and French versions of the discussions and decisions of the Conference would be acceptable to members of the Conference. It was further agreed that the term "tropic" might, if necessary, be used with appropriate modifications in translations into other languages.

It was agreed:

(3) That the Conference recommend the adoption, for general scientific use, of the term "gonadotrop(h)in" for reference to principles with gonadotrophic action, with the addition, in each case, of a suitable adjective or descriptive phrase, to indicate the source of origin of the particular principle to which reference is made.

(4) That the Conference recommend the adoption, for general use, of the terms "corticotrop(h)in" and "thyrotrop(h)in," to denote the active principles of the anterior lobe of the pituitary gland acting on the adrenal cortex and on the thyroid gland, respectively.

British Standards Institution

THE following Standard Specifications have been issued†:

No. 838—1939. BRITISH STANDARD METHOD OF TEST FOR THE TOXICITY OF WOOD PRESERVATIVES TO FUNGI.

The most important of the factors upon which the efficacy of a wood preservative depends are:—(1) toxicity to wood-destroying fungi; (2) penetrating power; (3) permanence. The present Specification deals only with toxicity, and stress is laid upon the fact that it is not possible to estimate from toxicity tests alone the value of a wood preservative when exposed out-of-doors to the influence of the weather.

Attempts have recently been made to standardise two types of toxicity tests: (1) the so-called agar or Petri dish method (Schmitz *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, 1930, **2**, 361), and the wood-block method, for which an international standardised method has been prescribed (Liese *et al.*, *Z. angew. Chem.*, 1935, [21], 48). The relative value of the two methods has been studied by Findlay (*Ann. Appl. Biol.*, 1932, **19**, [2], 271), who concludes that the agar test gives only preliminary results. It is of value for comparing the toxicities of substances of similar character, *e.g.* phenols, but gives erroneous results with substances differing widely in chemical composition. At the Berlin Conference the wood-block method was considered the most suitable means for estimating the toxicity of a wood preservative to fungi, and this method is recommended for adoption as the British Standard Method.

The Specification gives an outline of the principles of the test, and a description, with dimensions, of the standard (Kolle) culture flask proposed by the International Committee. The flask used at the Forest Product Research Laboratory is somewhat larger, and has a reservoir in the neck for water. The standard medium consists of 50 g. of malt extract (B.P. quality) and 20 g. of agar per litre. About 40 ml. of this medium are sterilised in the culture flask for 20 minutes at 15 lb. gauge pressure, or by steaming at atmospheric pressure for 30 minutes on each of three successive days. The medium is inoculated with the test fungus within a few days after preparation, and the test blocks are infected by placing them over the cultures in the flasks in such a way that the wood comes in contact with the aerial mycelium but not with the medium itself.

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* *Bulletin of the Health Organisation of the League of Nations*, Vol. VII, Extract No. 32, pp. 898–899.

† Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. each net, post free 2s. 2d.

The test fungi employed are: *Coniophora cerebella* Pers. (Idaweiche strain); *Lentinus lepideus*, Fr. (= *L. Squamosus*), which is particularly resistant to tar preservatives; *Poria vaporaria* (Pers.), Fr. (Eberswalde strain); for tests on beech, *Polystictus versicolor* (Linn.), Fr., should be employed.

The species of wood ordinarily used are: (1) the sapwood of Scots pine (*Pinus sylvestris*, and (2) the outer wood (*i.e.* within 3 in. of the inside of the bark) of beech (*Fagus sylvatica*). The blocks (of standard dimensions) are dried, sterilised for about 18 hours in an oven at 100°–105° C., and weighed as aseptically as possible to the nearest centigram ("initial weight"), after which they are impregnated for about 2 hours with the preservative under reduced pressure, then allowed to drain for not longer than one minute, and again weighed. The concentration of preservative is calculated as kg. per cb. metre of wood. The test blocks are exposed to fungal attack for three months, and the amount of decay is calculated from the loss in dry weight of the wood, determined under specified conditions.

The Specification gives examples of toxic limits (kg. per $m.^3$) obtained with samples of creosote and commercial sodium fluoride, and an example of evaluation of test results.

No. 839—1939. British Standard Specification for Veterinary Cod-liver Oil.

This Specification forms part of a series of British Standards for Marine Animal and Fish Oils, the preparation of which was authorised by the Chemical Divisional Council.

For the purpose of the Specification, Veterinary Cod-liver Oil is defined as the product obtained from the fresh, iced or otherwise suitably preserved livers of the cod, *Gadus morrhua* Linn, and other species of *Gadus*.

The oil, when kept for 24 hours at a temperature of 16° C., shall be a clear yellow liquid and shall be free from any foreign matter. The odour shall be slightly fishy but not rancid, and the taste shall be bland and slightly fishy.

Colour.—The colour of the oil, filtered at 20° C., when measured through a 1-in. cell, shall be not deeper than a colour equivalent to a combination of 12 yellow and 2·7 red units on the Lovibond colour scale. (*Note.*—The number of glasses shall be the same on each side of the Lovibond instrument, colourless glasses being placed in front of the oil to secure this if necessary.)

Specific gravity and density.—The sp.gr. of the oil at 15·5°/15·5° C. shall not be lower than 0·922 nor higher than 0·929. Densities at 20° C. (*i.e.* weight in air of unit volume of oil) may be obtained by subtracting 0·0018 from the corresponding sp.gr. at 20° C.

Refractive index.—The value for the D line at 20° C. shall be not lower than 1·478 nor higher than 1·482.

Iodine value.—This shall be not lower than 150 nor higher than 178 when determined by the Wijs method.

Saponification value.—When determined in the specified manner this shall not be lower than 180 nor higher than 190.

Acidity.—The acidity (expressed as per cent. of oleic acid) shall not exceed 1 per cent. unless otherwise declared, and in any event shall not exceed 3 per cent. when determined by the specified method.

Unsaponifiable matter.—The oil shall not contain more than 1·5 per cent., unless otherwise agreed, and in no case more than 1·7 per cent., as determined by the Society of Public Analysts' method.

Vitamin potency.—The vitamin potency of the oil shall be not less than 500 units of vitamin A per gramme, and 50 units of vitamin D per gramme. All declarations of vitamins A and D potencies shall be made in International units per gramme, and the oil shall be tested for vitamin potencies in accordance with the specified methods (B.P. 1932, pp. 86–91; pp. 597–600, incorporating amendments in Addendum 1936 to B.P. 1932).

Blue value.—If the oil is submitted to the antimony trichloride test described (based on the B.P. method, 1932, pp. 596–7, and deleted by the Addendum, 1936), the blue value shall not be lower than 6. If the blue value of the oil is declared, it shall have been carried out by the method described.

The blue value of Veterinary Cod-liver Oil is not to be taken as a measure of the vitamin A content, but only as an approximation thereto. If a discrepancy arises between the vitamin A values suggested by this method and by the biological method, the value determined by the biological method shall be accepted.

Sampling and size of sample.—Representative samples, each measuring not less than 400 ml., shall be taken, wherever possible in triplicate, from original containers or from the bulk, and shall be packed in clean, dry, air-tight, non-absorbent containers, on which the sample has no action. The containers shall be of such size that they are nearly filled by the sample. Each sample container so filled shall be marked with full details and date of sampling.

Recommended methods for sampling fats and fatty oils, are given in B.S. 627.—1935.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of the Volatile Products Liberated from Stored Fruit. F. Gerhardt and B. D. Ezell. (*J. Agric. Res.*, **1939, 58,** 493–503.)—Acetaldehyde, identified as one of the more common and abundant volatile products of fruit metabolism, has been taken as representative of the odorous constituents formed in a specific type of physiological metabolism under the conditions of handling practice or storage temperature. The method used for the determination of the total oxidisable volatile compounds emanating from stored fruit was based on their absorption in conc. sulphuric acid, oxidation with ceric sulphate and evaluation in terms of ceric sulphate reduced. Small absorption towers filled with glass beads and fitted with 250-ml. extraction flasks were used as gas scrubbers, the flasks were charged with 25 ml. of sulphuric acid, and the volatile substances were conveyed in an air-stream of 10 litres per hour. After the absorption the beads were rinsed with 75 ml. of water into the extraction flasks, $N/10$ ceric sulphate solution was added (50–100 ml.), and the flasks were heated over a boiling water-bath for 2 hours, after which their contents were transferred to 500-ml. flasks and made up to the mark. Aliquot portions (100 ml.) were diluted with 250 ml. of water, 0·3 to 0·5 g. of potassium iodide was added, and the solutions were titrated with $N/10$ sodium thiosulphate solution. The average recovery of acetaldehyde was 97·2 per cent. Applications of the method included measurements of the volatile substances in air from various stores, inter-relation of respiration and liberation of volatile substances from Golden Delicious apples, and the influence of certain fruit-rot fungi on the emanation of volatile substances. D. G. H.

Bromide-Content of Fruits and Vegetables following Fumigation with Methyl Bromide. H. C. Dudley. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 259–261.)—The samples were fumigated for 2 to 24 hours at atmospheric pressure and at 20° to 25° C. with 2 lb. of methyl bromide in 1000 cb.ft. of air. Tests for bromide were made immediately afterwards and also at intervals after exposure to fresh air. The samples absorbed up to 6 or 7 mg. of methyl bromide per 100 g., but generally much of this was lost in 48 hours after fumigation. The following are examples from the results.

	Mg. Bromine per 100 g.		
	before fumigation	immediately after	48 hours after
Green beans	0·54	7·22	4·08
Dried peaches	1·44	2·31	1·60
Apples (fresh)	none	0·30	0·27

The method of determination involved digestion of the sample with alcoholic potash, followed by evaporation and ashing of the residue; bromine was liberated by a chromic-sulphuric acid mixture, carried over by air aspiration into potassium iodide solution, and determined by titration with thiosulphate, on the lines of the method of Baughman and Skinner (*Ind. Eng. Chem.*, **1919, 11,** 954; Abst., ANALYST, **1919, 44,** 417). S. G. C.

Methods of Analysis of Molasses used in the Fermentation Industries. W. A. Davis. (Research Labs., Distillers Company, Ltd., Epsom, pp. 16.)—This description of methods adopted in the Research Department of the Distillers Company is published as "a contribution to the unification of methods of sugar analysis." For distilleries the value of a molasses depends mainly on the yield of alcohol obtainable from it in practice. A procedure for determining this by a fermentation test, occupying a number of days, is described. Methods are described also for determining, by ordinary analysis, the content of total sugars, but this is not a satisfactory measure of the yield of alcohol, as it includes a variable proportion of unfermentable sugars ("glutose"), the amount of which, calculated as invert sugar, has been found to range from 3 to 6 per cent. in blackstrap molasses, from 2 to 3 per cent. in "high-test" molasses (containing 70 to 80 per cent. of total sugars) and from 0·4 to 1 per cent. in beet molasses. These percentages probably represent about twice as much in actual material, for the reducing power of the unfermentable sugars is probably only about half that of invert sugar, but it is usual to express them in terms of invert sugar. The proportion of unfermentable sugars is variable even amongst molasses of the same type; the judging of distilling value from the content of total sugars therefore demands caution and experience. A useful value described is the *fermentation value*, defined as the actual yield of alcohol, expressed as a percentage of the yield theoretically obtainable if the total sugars present (after inversion) could be transformed in accordance with the equation: $C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$; this value may range between 80 and 90 per cent.

Determination of Total Sugars.—Reducing methods only are used, polarimetric methods being considered less accurate with molasses. Reducers are determined as invert sugar with Fehling solution, before and after inversion. Inversion is carried out on 1 per cent. solutions, under Clerget–Herzfeld conditions but with 10 minutes' total heating in a bath at 70° C. The molasses solutions are not clarified before analysis, on the ground that without clarification the results are sufficiently close to those obtained after clarification with neutral lead acetate followed by de-leading and decalcification with potassium oxalate (*cf.* Eynon and Lane, *J. Soc. Chem. Ind.*, 1923, 466T). For the determination of total sugar as invert sugar after inversion, the Lane–Eynon method is used, with 10 ml. of Fehling solution and a sugar concentration of 0·2 to 0·3 per cent. For the determination of invert sugar before inversion, when the proportion in the molasses exceeds 20 per cent., the same method may be used or alternatively the Brown, Morris and Millar gravimetric method (Allen's *Commercial Organic Analysis*, 5th Ed., Vol. I, 397). With molasses containing less than 20 per cent. of invert sugar (and therefore with all beet molasses) this original invert sugar is always determined by the Brown, Morris and Millar method. This determination is carried out on 50 ml. of 1 per cent. molasses solution, and the precipitated cuprous oxide, collected in a Gooch crucible, is oxidised by moderate ignition and weighed as cupric oxide. If the weight (corrected by a blank) is less than 0·245 g. it is multiplied by 81·5 to obtain the percentage of invert sugar in the molasses; the calculation for larger weights of cupric oxide is in accordance with the Table of Brown, Morris and Millar.

Determination of Spirit Yield and Unfermentable Sugars.—A solution of 200 g. of blackstrap (or 150 g. of high-test) molasses in about 400 to 500 ml. of tap-water is adjusted to *p*H 4·4–4·6 (high-test to *p*H 4·9 to 5·1) with sulphuric acid (usually 15 to 20 ml. of 2 *N* acid for 200 g. of cane molasses, and 0 to 4 ml. for 150 g. of high-test molasses) and treated with 25 ml. of 4 per cent. diammonium phosphate solution adjusted to *p*H 5 with sulphuric acid. The liquid is diluted to 1 litre and weighed. Two 400-ml. lots are weighed into two 750-ml. conical flasks. Four drops extra are then added to each, and from each flask 2 ml. are pipetted into a test-tube and 20 ml. into a 100-ml. conical flask. These (four) small receptacles are then plugged with cotton wool and they, and the 750-ml. flasks fitted with empty liquid traps (to contain conc. sulphuric acid later), are sterilised by steaming. When cooled, the test-tubes are seeded with a pure culture (agar slope) of the yeast actually employed in the distillery, and after incubation at 33° C. for 24 hours their contents are transferred to the 100-ml. flasks, which are similarly incubated and their contents after 24 hours transferred to the 750-ml. flasks. These, closed by their traps, into which 2·5 ml. of conc. sulphuric acid are introduced, are weighed to 0·01 g. and incubated at 33° C. Each is re-weighed after 3 days and then day by day until the loss in 24 hours does not exceed 0·05 g. After cooling, the acid from the trap is poured into a small flask containing ice, and nearly neutralised with 5·0 ml. of 50 per cent. sodium hydroxide solution, and it is then added to the fermented liquid, which is made up to 500 ml. On an aliquot part (100 ml.), alcohol is determined pycnometrically after being carefully distilled twice, first from the somewhat acid liquor, and again after being made slightly alkaline with sodium hydroxide. Duplicate results agree to within about 1 in 500 of the alcohol found.

To determine unfermentable sugar, a further aliquot part of the final fermented solution is neutralised and, after addition of alumina cream, filtered, and the apparent invert sugar is determined by the Brown, Morris and Millar method. Pentoses and pentosans may be determined by Kröber's method (*id.* p. 498) on a portion of the same filtered solution after removal of alcohol by evaporation.

Identification and Determination of Lactic Acid in Alcoholic Fermented Liquids. M. Niculescu. (*Z. anal. Chem.*, 1939, **116**, 175–183.)—The application of three methods to the detection of lactic acid in fermented liquids was studied. The reaction of Denigès (*Z. anal. Chem.*, 1911, **50**, 189), in which the lactic acid is converted by treatment with conc. sulphuric acid into aldehyde, which is identified by its reaction with guaiacol, was found to be unsuitable in the presence of small amounts of dextrose which invariably accompanied the lactic acid separated by extraction with ether. Detection by conversion into zinc lactate also proved unsuitable, since the crystals were never typical, owing to the presence of other substances. The reaction of Uffelmann (*Z. anal. Chem.*, 1888, **27**, 543), although not specific, was found most suitable for the detection of lactic acid separated from fermented liquids by extraction with ether. The reagent is prepared immediately before use by mixing 10 ml. of 4 per cent. phenol solution with 20 ml. of water and one drop of ferric chloride solution. Its amethyst-blue colour becomes yellow in presence of lactic acid. Gravimetric methods depending upon conversion into the zinc or calcium salt, volumetric methods depending upon titration of the separated acid, and optical methods were all found to involve appreciable errors caused by impurities in the separated lactic acid. The method finally recommended is based upon that of Fürth and Charnass (*Biochem. Z.*, 1910, **26**, 199), as modified by Tanaka and Endo (*ibid.*, 1929, **210**, 120), in which the lactic acid is oxidised to aldehyde, which is determined by an iodimetric method. The solution, containing about 5 mg. of lactic acid, is mixed with 35 ml. of 10 per cent. sulphuric acid and diluted to 150 ml. with water. After addition of a little talc, the mixture is heated in a flask provided with a dropping funnel and connected through a vertical water-condenser with a long-stemmed adapter leading into a filter-flask, the stopper of which also carries a tube through which sodium bisulphite solution can be introduced from a burette. The side-tube of the filter-flask is joined by rubber tubing carrying a screw-clip to a long tube bent twice at right angles and dipping into water, which acts as a seal. While the liquid in the distillation flask is being heated, sodium bicarbonate solution is run in slowly from the dropping-funnel until by the time boiling has begun the air in the apparatus has been replaced by carbon dioxide. A measured amount of sodium bisulphite solution (2·5 g. dissolved in a litre of water saturated with carbon dioxide) is delivered into the filter-flask from the burette until the outlet of the adapter is immersed. When the liquid begins to boil potassium permanganate solution (approx. 0·005 *M*) is run, drop by drop, from the dropping-funnel into the boiling solution until a pink colour persists. Distillation is continued for 30 minutes, any tendency of the bisulphite solution to rise in the adapter being checked by the cautious addition of sodium bicarbonate solution through the dropping-funnel. When distillation is complete the filter-flask is disconnected from the adapter (which is rinsed with a little water) and closed by means of a stopper and the screw-clip, the tube leading to the water-seal being removed. The liquid is agitated frequently during 30 minutes to promote reaction between the aldehyde and the bisulphite solution, and the uncombined sodium bisulphite is finally titrated with $N/100$ iodine solution, starch being used as indicator. The titre of the bisulphite solution is then determined, and the difference corresponding with the sodium bisulphite equivalent to the aldehyde formed is calculated into lactic acid. The method differs from that of Tanaka and Endo (*loc. cit.*) in that the sodium bisulphite solution is not introduced into the apparatus until all the air has been expelled. It was found that if the air is expelled through the bisulphite solution, oxidation occurred and erroneous results were obtained. Before its determination the lactic acid must be separated from the fermented liquid. Volatile substances are removed by steam-distillation and the residue, suitably concentrated, is kneaded into a firm mass with calcium sulphate and extracted with ether in a Soxhlet apparatus. Alternatively, the fermented liquid may be treated with finely powdered ammonium sulphate, allowed to stand for 24 hours, filtered, acidified with dilute sulphuric acid and extracted five times with the same portion of amyl alcohol, the lactic acid being recovered from the amyl alcohol after each extraction by means of 2 per cent. sodium carbonate solution. The combined sodium carbonate extracts are mixed with a little dimethylamidoazobenzene indicator, slightly acidified with dilute sulphuric acid and exactly neutralised with sodium carbonate solution. Suspended amyl alcohol and the indicator are then removed by steam-distillation. This method is rapid, but extraction with ether in a Soxhlet apparatus gives somewhat higher and more accurate results. A. O. J.

Oxidation in Beers. I. Simplified Method of Measurement. P. P. Gray and I. Stone. (*J. Inst. Brewing*, 1939, **45**, 253–263.)—The probability of a correlation between the stability of a beer and its *r*H value is discussed (*cf.* De Clerck, *id.*, 1934, **40**, 292, 407). It is concluded that such a relationship might be misleading, inasmuch as the *r*H value is derived theoretically from ideal, thermodynamically-reversible systems of known characteristics and in a state of delicate equilibrium, and with beer these conditions are not fully satisfied. Moreover, the usual electrometric technique is unsuitable for ordinary routine control in the brewery, and a simple colorimetric method which, it is considered, represents an empirical approximation of the oxidation-reduction capacity is preferred. The principle used is the measurement of the rate of partial (80 per cent.) decolorisation of a suitable indicator (*cf.* Hartong, *id.*, 1935, **41**, 116; *Wallerstein Lab. Comm.*, 1937, No. 1, 5). Sufficient gas is removed from the beer to eliminate excessive frothing, and three 10-ml. portions at 25° C. are placed in similar test-tubes, distilled water being introduced into two similar tubes. In a sixth tube are put 0·05 ml. of a 0·005 *M* solution of the indicator (see below), and 10 ml. of a phosphate buffer solution of *p*H 4·4; 0·25 ml. of the indicator solution is then put into one of the tubes containing the sample, the contents are mixed rapidly, and a stop-watch is at once started. The tubes are placed in a "block" type comparator, so that the three holes in the back row contain tubes of (1) water, (2) water, and (3) the indicator plus buffer, respectively, whilst in the corresponding holes in the front the tubes contain (1) beer, (2) beer plus indicator, and (3) beer, respectively. The time in seconds (known as the "indicator time test" or *I.T.T.*) is noted when the colour of the light transmitted by the centre pair of tubes (containing beer plus indicator and water) matches that transmitted by the pair containing indicator plus buffer and beer. The other pair of tubes serve as a visual aid to colour matching. The indicator is prepared by weighing out a little more than 150 mg. of the powdered sodium salt of 2.6–dichloro-benzenone-indophenol, and stirring this thoroughly with hot water; when cold, the solution is diluted to 100 ml. and filtered through a No. 40 Whatman paper. It is then standardised by titrating a mixture of 10 ml. of solution, 4 ml. of a freshly-prepared 25 per cent. solution of potassium iodide, and 2 ml. of dilute sulphuric acid (1 + 6) with 0·01 *N* sodium thiosulphate solution, and starch as indicator. The concentration, in mg., of indicator per 100 ml. of solution is obtained by multiplying the titration volume by 14·5, and this figure is used to adjust the strength of the solution of indicator to 145 mg. per 100 ml., *i.e.* approximately 0·005 *M*. The indicator should be kept in small, completely-filled and stoppered glass bottles, which are stored in a refrigerator, and it should be prepared every week, and standardised when required for use. For convenience in control work permanent colour standards may be used, as these keep for at least a year if sealed in Pyrex test-tubes and stored in the dark. They are prepared from (*a*) a solution of 5·0 g. of roseo-cobaltic chloride, $[CoCl_3(NH_3)_5,H_2O]$, and 100·0 ml. of conc. ammonium hydroxide in sufficient water to make 1 litre; (*b*) a solution of 5·0 g. of crystalline copper sulphate and 100·0 ml. of conc. ammonium hydroxide in sufficient water to make 1 litre. Colours corresponding with 80 and 50 per cent. decolorisation of the indicator are prepared by mixing 230 ml. of (*a*) with 70 ml. each of (*b*) and conc. ammonia; and from 540 ml. of (*a*) and 150 ml. of (*b*) with 31 ml. of conc. ammonia (see below), respectively. The former corresponds with the desired end-point. The characteristics and method of standardisation of the indicator selected have been investigated in connection with the determination of vitamin C. Since the oxidation-reduction potential range within which it is decolorised is well above that of beer, those constituents of beer which are susceptible to oxidation by air act as reducing agents towards it; the rate at which this occurs is the value required, and corresponds with the state of oxidation of the beer. The results are not affected immediately by dissolved oxygen, owing to the high oxidation-reduction potential range. The *I.T.T.* values for different beers range from 50 to over 3000 seconds, and a close connection has been traced between them and the colloidal stability and changes in flavour of the beers. Thus, beers which have been bottled with air develop oxidation hazes and have *I.T.T.* values which increase in time as such oxidation proceeds (*cf.* Wallerstein, *loc. cit.*). A logarithmic relationship was found to exist between the *I.T.T.* value and results obtained by the usual method for the colorimetric determination of the *r*H value (*cf.* Laufer, *J. Inst. Brewing*, 1936, **42**, 141). The slope of the curve is such that an *r*H range of 12 to 16 corresponds with an *I.T.T.* range of 50 to 3000 seconds, and this indicates the sensitive nature of the present test; moreover, unlike the other methods it does not necessitate a waiting period of 24 hours before making the test, so that the results can indicate the condition of the beer at any desired time. The indicator used varies in colour with the *p*H, being red at *p*H 4·6 and blue at *p*H 6·0; the use of a buffer solution (see above) is therefore necessary, and the value of 4·4 is chosen because it corresponds with that of beer itself. Higher values should be used for worts, although data are given which show that within the normal range of *p*H values encountered in brewing operation (3·2 to 5·8) as produced by the addition of acid or alkali to beer, the variation in the *I.T.T.* value falls within the limits of experimental error. Data also show that there is a linear relationship between the percentage decolorisation of the indicator and the logarithm of the time for which it is allowed to react. Hence with highly-oxidised samples (which have very low *I.T.T.* values) it is more convenient to measure the time required to decolorise the indicator to the extent of 50 per cent. and to find the 80 per cent. value (*i.e.* the *I.T.T.* value) by extrapolation; the average extrapolation factor, as obtained from the graphs, is then 7. For such samples the comparison standard is prepared by adding 0·125 ml. of indicator to 10 ml. of buffer solution, and the corresponding permanent colour standard is given above.

J. G.

Direct Determination of Chloride in Wine and its Occurrence in Bavarian and other Wines. H. Grohmann. (*Z. Unters. Lebensm.*, 1939, **77**, 482–488.)—The wine (100 ml.) is treated with 50 ml. of cold saturated barium hydroxide solution, diluted with water to 200 ml. and filtered, and 100 ml. of the filtrate are treated with 20 ml. of dilute nitric acid (1 : 5) and 2 or 3 ml. of saturated potassium permanganate solution. After a few minutes, when the violet colour will have disappeared, the mixture is treated with 2 ml. of 3 per cent. hydrogen peroxide solution, which causes complete decolorisation. After the addition of 10 ml. of 10 per cent. ferric nitrate solution (ferric alum cannot be used in the presence of barium) and 20 ml. of ether (which promotes curdling of the silver chloride), $N/10$ silver nitrate solution is added and the excess is titrated with $N/10$ potassium thiocyanate solution in the usual manner until a red colour persisting for at least 5 seconds is formed. The accuracy of the method was established by the addition of known amounts of sodium chloride to wines of known chlorine-content. Authentic samples of wine from the Bavarian Palatinate were examined by this method. For red wines (18 samples) the chlorine-content varied from 22·7 to 85·1 mg. per litre, and for white wines (91 samples) from 14·2 to 138·3 mg. per litre, and in only 5 of these 109 samples did the chlorine-content exceed 90 mg. per litre. The range for Bavarian wines may therefore be taken as 10 to 90 mg. per litre and the values found by Halenke and Möslinger (König, *Chemie der menschlichen Nahrungs- und Genussmittel*, **2**, 1288) are confirmed. No explanation can be suggested for the high values shown by a few individual samples. The presence of more than 150 mg. of chlorine per litre may be regarded as a definite indication of adulteration either by the addition of substances containing chloride or by admixture with other wine. The chlorine-content of a number of foreign wines varied from 106·4 to 595·6 mg. per litre. The reason for these high values is not known. It has been suggested that they may be due to the use of grapes grown in an excessively saline soil, to deposits on the grapes of salt from wind laden with sea-spray, to the use of pest-control materials prepared from sea-water, or to absorption of salt from casks which have been filled with sea-water. In the literature the chlorine-content of wine is frequently expressed as sodium chloride, and Merz (*Wein und Rebe*, **10**, 103) suggests that the chlorine-content may be inferred from the sodium-content. Determinations of the sodium-content by the method of Reichard (*Z. Unters. Lebensm.*, 1936, **71**, 501) showed that sodium and chlorine are not present in equivalent amounts in wine. A. O. J.

Brandy. P. Valaer. (*Ind. Eng. Chem.*, 1939, **31**, 339–353; *J. Inst. Brewing*, 1939, **45**, 266–267.)—The manufacture, characteristics and composition of brandies prepared from various fruits in America and other countries are discussed. Three classes of brandy are manufactured in California:—(*a*) fortifying brandy, which is distilled to a proof-content of 180 to 190 per cent. (U.S.A.) and stored in metal drums; (*b*) commercial beverage brandy, which is distilled below 175 per cent. proof and stored in barrels at 102 per cent. proof; (*c*) "grappa" brandy prepared from pressed pomace which, after a long secondary fermentation, is mixed with grape residues, lees, etc., and distilled to yield less than 160 per cent. proof. American grape brandy is distilled in continuous stills, and then coloured with caramel and matured in new white-wood casks, whilst brandies from other fruits (and especially from apples) are usually prepared in pot stills and aged in charred-wood casks. All genuine brandies contain a little methyl alcohol, *viz.* less than 0·05 and about 0·10 per cent. in grape and other fruit brandies, respectively. The esters, however, are the most important constituents. They are present in brandy in greater proportions than in any other spirit, and determine the flavour and general characterisitics of the product. In the maturing process ethyl acetate is produced the most rapidly and most abundantly, but the higher esters, although they are formed more slowly, are more important from the point of view of flavour. American grape and other fruit brandies differ from French cognac in that they have the aroma of the original fruit with an unmistakable natural flavour which is enhanced by maturation, whilst the flavour of cognac bears no resemblance to that of the fruit from which it is derived. French brandies contain about 0·02 per cent. of a clear yellow oil having a powerful odour of cognac; this is a natural ingredient and is absent from all other types of brandy. The flavour of brandy is the most important characteristic which determines its quality, but it is affected adversely by the use of impure water, and by contact with certain metals and unsuitable wooden containers. J. G.

Nicotine from Tobacco. C. Pyriki. (*Z. Unters. Lebensm.*, 1939, **77**, 379–385.)—It has been observed (Waser and Stahli, *Z. Unters. Lebensm.*, 1932, **64**, 740; Pyriki, *Pharm. Zentralh.*, 1933, **74**, 253; Hammerle and Weber, *Mitt. Lebensmittelunters.*, 1936, **27**, 46) that when tobacco is steam-distilled with magnesium oxide until no further nicotine is evolved, an additional evolution occurs if distillation is continued after the addition of sodium hydroxide or potassium carbonate. This evolution, which occurs somewhat slowly, can be hastened by the addition of hydrogen peroxide to the alkaline liquid. The present work was undertaken to determine what portion of the total nicotine obtainable is originally present in the tobacco and what portion is produced by decomposition of other substances. Experiments were made with finely powdered Kentucky and Java tobacco. An aqueous extract of each variety was steam-distilled after the addition of sodium chloride and sodium hydroxide until the distillate was free from nicotine, as indicated by the reaction with silicotungstic acid. Distillation was continued, and the distillate now obtained was acidified, concentrated, treated with picric acid, and left for four weeks in an ice-chest to promote the deposition of nicotine dipicrate. Only a very small amount of the dipicrate was obtained. After the lapse of one month the alkaline liquid was again distilled and the dipicrate was prepared; a considerable amount was now obtained. This procedure was repeated at monthly intervals until 19 fractions had been obtained from each variety of tobacco. The fractions were combined, and the dipicrate was purified by recovery of its nicotine, which was re-converted into the dipicrate. Nicotine was again liberated from the pure dipicrate by distillation with magnesium oxide, and by determination of its optical rotatory power in toluene solution it was proved to consist mainly of inactive racemic nicotine. This was confirmed by the determination of the m.p. of its picrolonate, which was 232·5 to 233° C., whereas the m.p. of *l*-nicotine picrolonate is 223° to 224° C. Control experiments with pure *l*-nicotine subjected to the same procedure showed that it suffered no change either in its optical activity or in the m.p. of its picrolonate. It is concluded therefore that the additional nicotine obtained gradually by the prolonged action of alkali is not present in the original tobacco, but is produced by the decomposition of other substances. An extract prepared from Kentucky tobacco was distilled with sodium chloride and magnesium oxide. When the distillate gave only a slight turbidity with silicotungstic acid (fraction A) the receiver was changed and distillation was continued until the distillate ceased to answer to the test (fraction B). The residue was now made strongly alkaline with sodium hydroxide solution and distilled in steam until the reaction of the distillate with silicotungstic acid was again feeble (fraction C). Finally the distillation was continued with periodic addition of hydrogen peroxide until the distillate was again free from nicotine (fraction D). By determination of the m.p. of the dipicrates and picrolonates prepared from these fractions and of the optical activity of the fractions of nicotine recovered from them, it was found that A consisted of *l*-nicotine, that B was a mixture of other alkaloids volatile with difficulty, that C contained *l*-nicotine and nor-nicotine and that the nicotine in D was the racemic mixture resulting from decomposition of other constituents of tobacco. The final conclusion drawn was that the additional nicotine obtained by distillation with sodium hydroxide after the preliminary distillation with magnesium oxide was originally present in the tobacco and was not derived from other substances. Distillation with sodium hydroxide will therefore give the total nicotine-content of the tobacco. The nicotine obtained by prolonged action of sodium hydroxide (or more rapidly by distillation with sodium hydroxide and hydrogen peroxide) is mainly a racemic mixture formed by decomposition of other substances. If the tobacco contains other volatile alkaloids, these will appear both in the distillation with magnesium oxide and in that with sodium hydroxide. Their separation may be effected by the method of Koenig and his collaborators (Bömer, Juckenack and Tillmans, *Handbuch der Lebensmittelchemie*, 6th Ed., p. 296, Berlin, 1934).

A. O. J.

New Coupling Component for Sulphanilamide Determination. A. C. Bratton and E. K. Marshall. (*J. Biol. Chem.*, 1939, **128**, 537–550.)—Of 17 compounds examined as coupling agents for the estimation of sulphanilamide, N-(1-naphthyl)-ethylenediamine dihydrochloride was selected because it can be prepared in a highly pure state; it couples very rapidly, and the process is not influenced by *p*H in the range of 1 to 2. Further, the colour of the dye is not affected by variations of *p*H within this range, and the dye itself is very soluble. Two ml. of oxalated blood are measured into a flask, diluted with 30 ml. of 0·05 per cent. saponin solution, and after 1 or 2 minutes treated with 8 ml. of 15 per cent. trichloroacetic acid solution. The precipitate is filtered off, and 1 ml. of 0·1 per cent. sodium nitrite solution is added to 10 ml. of the filtrate, followed after 3 minutes by 1 ml. of 0·5 per cent. ammonium sulphamate solution, and after a further 2 minutes by 1 ml. of a 0·1 per cent. solution of N-(1-naphthyl)-ethylenediamine dihydrochloride. A comparison, within an hour, of the colour produced with that of an appropriate standard obtained by a similar procedure gives an estimate of the amount of free sulphanilamide in the blood. To estimate the total sulphanilamide, 10 ml. of the filtrate are treated with 0·5 ml. of 4 *N* hydrochloric acid, the mixture is heated in a boiling water-bath for 1 hour and then cooled, and the volume is adjusted to 10 ml. The subsequent procedure is as described above. To estimate sulphanilamide in urine, the protein-free sample is diluted so as to contain 1 to 2 mg. per 100 ml., and 50 ml. of this diluted urine, plus 5 ml. of 4 *N* hydrochloric acid, are diluted to 100 ml. Ten ml. of this solution are treated as a blood filtrate for the determination of free sulphanilamide, and another portion of 10 ml. is treated for total sulphanilamide. If the urine contains protein, it is diluted and treated by the procedure for blood. The estimations can also be made with the aid of a photoelectric colorimeter, dilutions of blood (with water, saponin being unnecessary) of 1 : 50 or 1 : 100 being used. A filter, transmitting the maximum of light at 545$m\mu$ (the absorption maximum of the dye formed) must be used. Sulphanilamide can be estimated by this method in body fluids other than blood or urine. When tissues are to be analysed, the ground material is extracted in a Soxhlet apparatus with alcohol, and the extract is suitably diluted with water. Any sulphanilamide with a primary amino group or with a group convertible into one by hydrolysis, can be estimated, but high dilutions have to be used with sparingly soluble substances. The recovery of sulphanilamide itself added to blood was practically quantitative from a 1 : 50 dilution of the blood, but was only 90 per cent. complete from a 1 : 4 dilution. F. A. R.

Biochemical

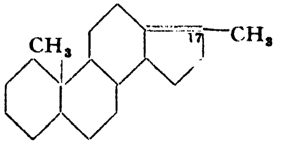
Biochemical Importance of Unsaturated Fatty Acids. S. Skraup, F. Strieck and J. Schorn. (*Z. physiol. Chem.*, 1939, **259**, 1–18.)—The administration of natural fats to experimental animals is usually followed by a characteristic fall in the respiratory quotient, but when glycerides of fatty acids having an odd number of carbon atoms were fed to dogs, the respiratory quotient showed no such fall, nor was the amount of heat produced increased. The heat production did increase, however, when an unsaturated glyceride, for instance, triolein or the glyceride of heptadecenoic acid, was given together with the "odd" glycerides, showing that the fat was being metabolised more rapidly; the unsaturated glyceride alone did not increase the amount of heat produced. The "activator" function of unsaturated acids was confirmed by a different type of experiment in which groups of rats that had practically ceased growing were given saturated glycerides, with and without triolein. In nearly every instance the rats fed only with saturated glycerides lost weight, whilst those receiving also the unsaturated glycerides gained weight. The carcases of some of these rates were digested with sodium hydroxide solution and the fatty acids were isolated. It was found that more fat had been deposited in the rats receiving the saturated glycerides than in those receiving mixed glycerides, and that the fat from the former group of rats was more saturated than the fat from the latter. The experiments on dogs further showed that there was no significant difference between the accelerating effect of heptadecen-(8)-oic acid, oleic acid and nonadecen-(10)-oic acid, but that undecylenic acid and the acids of the elaidic acid series were inactive. The unsaturated acids are not catalysts in the accepted sense of that term; they are hydrogen acceptors, being themselves reduced—irreversibly—to saturated acids. It appears that the dictum "fat is burnt in the fire of carbohydrates" now requires the reservation that the unsaturated fatty acids serve as the "activators" or "initiators" of this fire.
F. A. R.

Connection between Taste and Constitution of Carboxylic Acid Hydrazides and their Derivatives. J. J. Blanksma and H. A. Bakels. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 497–513.)—The connection between taste and chemical constitution of malonyl and succinyl dihydrazides, the trihydrazide of citric acid, the hydrazides of ortho-, iso- and terephthalic acids and nuclear substituted 2-hydroxymethylbenzylhydrazides, was investigated. It was found that the sweet taste of malonyl dihydrazide disappeared on condensation with aldehydes and ketones, bitter substances being produced with acetone, methyl ethyl ketone and diethyl ketone, the taste being less pronounced the greater the size of the alkyl group. The acetyl derivative was also bitter. Similar results were obtained with the sweet tasting succinyl dihydrazide, whilst the very sweet trihydrazide of citric acid gave, on condensation with aromatic aldehydes and ketones, insoluble derivatives that were without taste. It was not found possible to prepare orthophthaldihydrazide; phthalhydrazide, which is tasteless, was obtained instead. Isophthal-dihydrazide and terephthaldihydrazide were found to be tasteless, but the two acetone derivatives were slightly bitter. The monomethylhydrazide and dimethylhydrazide of phthalic acid were tasteless. Phthalide, meconine and benzyl alcohol have bitter tastes; 6-nitro-phthalide was found to be less bitter than phthalide itself, whilst 6-amino-phthalide and 4-nitro- and 4-amino-meconine were tasteless. The 2-hydroxy-methyl-hydrazides obtained by treating meconine and phthalide with hydrazine also had bitter tastes, but benzhydrazide and its acetone and benzal derivatives were tasteless. Maximum bitterness was attained in this group with 5-nitro-2-hydroxy-methyl benzhydrazide. It thus appears that at least two $.CO.NH.NH_2$ groups must be present to produce a sweet taste, and that these groups must not be too far from one another in the molecule. A hydroxyl group apparently increases the sapophoric function of the hydrazine residue. Condensation of hydrazides with acetone in particular sometimes, but not always, results in bitter-tasting compounds. The introduction of a hydroxyl-methyl group also produces a bitter taste. F. A. R.

Micro-determination of Glutamic Acid. P. P. Cohen. (*Biochem. J.*, 1939, **33**, 551–558.)—Glutamic acid is converted by treatment with excess of chloramine-T into β-cyanopropionic acid, which is converted by acid hydrolysis into succinic acid; this can be estimated manometrically by means of a succinoxidase preparation. By employing the right conditions in the first two stages of this series of reactions, a quantitative conversion of glutamic acid into succinic acid is obtained. Glutamic acid can be determined in tissue slices without the necessity of de-proteinising, but suspensions of minced tissue must first be freed from protein by the addition of two-thirds of their volume of 2/3 *N* sulphuric acid and one-third of their volume of 10 per cent. sodium tungstate solution. The solution to be analysed is adjusted to *p*H 4·7 by the addition of 1 to 1·5 ml. of citrate buffer solution (17·65 g. of sodium citrate, $Na_3C_6H_5O_7.2H_2O$, and 8·40 g. of citric acid, $C_6H_8O_7.H_2O$, in 50 ml.), 2 ml. of 10 per cent. chloramine-T solution are added, and the solutions are well mixed. They are then shaken at 40° C. for ten minutes, after which the flasks are placed in an ice-bath for 15 to 20 minutes to cause the precipitation of the *p*-toluene-sulphonamide formed and the excess of chloramine-T. The solutions are filtered, the precipitate is washed with several small volumes of water, and the combined filtrate and washings are collected in large test-tubes. The solution is acidified with 4 ml. of 10 per cent. sulphuric acid and the β-cyanopropionic acid is extracted from the solution in a continuous extractor with ether. The contents of the flask are treated with 2·5 ml. of 0·1 *M* phosphate buffer solution (*p*H 7·4), and the ether is slowly distilled off. The remaining aqueous solution is then chilled to precipitate the *p*-toluenesulphonamide, which is filtered off. Sufficient conc. hydrochloric acid is added to the filtrate to bring the concentration of acid up to at least 12·5 per cent., and the tubes are then heated in a boiling water-bath for 15 minutes and cooled, and sodium hydroxide solution (50 to 60 per cent.) is added dropwise until the solution becomes hot. Then 0·5 ml. of 5 per cent. ammonium chloride solution is added to destroy traces of chloramine-T, and the solution is made alkaline to phenol red, a few drops of which are added to the solution. The remaining traces of *p*-toluenesulphonamide are removed by extraction in a continuous extractor with peroxide-free ether, after which the solution is made strongly acid to phenol red with 3 ml. of 10 per cent. sulphuric acid, and again extracted with peroxide-free ether. When the extraction of succinic acid is complete, 2 to 3 ml. of 0·1 *M* phosphate buffer solution are added to the ethereal solution followed by dropwise addition of 2 *N* sodium hydroxide solution until the reaction is neutral or slightly alkaline. The ether is distilled off, and the aqueous solution is concentrated to about 1 ml. and transferred with the aid of 0·5 to 2 ml. of 0·1 *M* phosphate buffer solution to a graduated flask. The succinic acid is then estimated according to the method of Krebs (*Biochem. J.*, 1937, **31**, 2095). The recovery of known amounts of glutamic acid from pure solutions varied from 91·5 to 98·2 per cent., and the recovery from protein solutions was of the same order. As little as 1 mg. of glutamic acid can be determined by the method, which is highly specific. No compound other than glutamine occurring in biological material has been found to react. F. A. R.

New Colour Reactions for the Steroids. H. Kägi and K. Miescher. (*Helv. Chim. Acta*, 1939, **22**, 683–697.)—On treating the two epimeric testosterones with bromine (or other halogen) in presence of a mineral acid, the *cis*, but not the *trans* compound, was found to give a red solution, and on examining a series of similar pairs of compounds the reaction was found to be a general one for all steroids possessing a 17-*cis* hydroxyl group, but no colour was obtained with the corresponding *trans* compounds. About 1 mg. of the substance is dissolved in 1 ml. of glacial acetic acid, and after the addition of 1 drop of conc. sulphuric acid the solution is warmed for a few seconds. It is then cooled and a 1 per cent. solution of bromine in acetic acid is added slowly, drop by drop. A blue to violet colour is usually produced, but this is destroyed by excess of bromine. Thus when only a small amount of material is available, as little as 10γ may often be detected if a very dilute solution of bromine is used. Instead of bromine, acetic anhydride can be employed with advantage, as an excess of that reagent is quite harmless. The formation of the colour depends on the dehydration of the carbinol, and these conditions, whilst adequate to remove the elements of water from *cis* compounds, are not sufficiently drastic to affect the *trans* compounds. The latter give colours, however, by the following procedure. About 1 mg. of the substance is dissolved in a mixture of 1 volume of phosphorus oxychloride and 3 volumes of quinoline, and the solution is warmed. After cooling, 1 to 2 ml. of glacial acetic acid and 2 to 3 drops of conc. sulphuric acid are added, and then a 1 per cent. solution of bromine in acetic acid, drop by drop. Under these conditions *trans* compounds give the same colour as the corresponding *cis* isomers give under the conditions employed in the first reaction. Thus a substance that gives a colour by the second reaction, but not by the first, almost certainly contains a 17-*trans* hydroxyl group.

A re-investigation of the Liebermann–Burchard reaction showed that this has a close connection with the new colour reaction. Thus blue to green colours are obtained with steroids that possess a *cis* hydroxyl group as well as with true sterols. The Liebermann–Burchard reaction is, however, much less characteristic than the new test and cannot be used to detect the presence and configuration of a 17-hydroxyl group. When androstan-17-ol was treated with potassium bisulphate or copper sulphate, a substance called pseudo-androstene was produced, which has been shown to have the following structure:



This, on treatment with a bromine solution in acetic acid containing a small amount of hydrobromic acid, gives a brown uncrystallisable resin, which dissolves in acetic acid to give a blue solution. This resin is probably a high-molecular, unsaturated compound, and is the prototype of the coloured substance produced in this reaction. F. A. R.

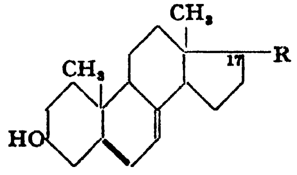
Colour Reactions of Steroids in Relation to Constitution. G. Woker and I. Antener. (*Helv. Chim. Acta,* 1939, **22**, 666–672.)—Digitoxigenin and gitoxigenin give characteristic colour reactions with furfural and conc. sulphuric acid. Thus when to a mixture of 1 ml. of a 0·25 per cent. alcoholic solution of digitoxigenin, 1 ml. of alcohol and 0·05 ml. of a 1 per cent. alcoholic solution of furfural is carefully treated with conc. sulphuric acid so that this forms an under-layer, a narrow, greenish-yellow, weakly fluorescent ring and a narrow orange-coloured ring are produced. These are due to the action of the sulphuric acid on the genin. At the same time a characteristic appearance of the contact-surface is produced; one-half is coloured dark violet, whilst the other half is occupied by lilac-coloured streaks. This effect is produced by the action of furfural and acid on the digitoxigenin, and is also characteristic of iso-androsterone. When 0·1 ml. of furfural solution is used instead of 0·05 ml., the contact-surface appears uniformly dark violet in colour with a slight bluish tinge. When a mixture of 1 ml. of alcohol and 1 ml. of the digitoxigenin solution is treated with conc. sulphuric acid, a bright yellow layer is formed at the bottom of the tube, with an orange ring above it, and at the top an olive or grass-green ring having a pronounced green fluorescence. The addition of sulphuric acid to a solution of gitoxigenin and furfural results in a cherry-red ring at the bottom due to the action of sulphuric acid on the genin, and above this a double ring, black below and olive-green above, due to the action of furfural on the gitoxigenin. This ring increases in thickness when the concentration of furfural is increased. When sulphuric acid is added to gitoxigenin solution only, a cherry-red ring is formed with an orange to bright red ring below it; this increases in thickness and intensity on standing, a pale rose-coloured zone gradually forming below and a narrow greenish-yellow ring above. F. A. R.

Determination of Vitamin B_1 by means of Yeast. K. Heyns. (*Z. physiol. Chem.*, 1939, **258**, 219–237.)—Six wide-necked 200-ml. bottles are each connected with a gas-burette containing water with a supernatant layer of paraffin oil to prevent solution of carbon dioxide. The bottles are immersed in a thermostat at 30° C., and by means of a suitable device are shaken throughout the experiment. Forty ml. of a medium consisting of a phosphate buffer solution (50 g. of $NH_4H_2PO_4$ and 30 g. of $(NH_4)_2HPO_4$ in 1 litre), containing glucose and salts, are measured into each flask, and the solution to be tested (after dilution to 40 ml.) is introduced; for the blank test, 40 ml. of water are used. The air in the entire apparatus is then displaced with carbon dioxide, and finally 20 ml. of a suspension containing 1 g. of pressed yeast are put into each flask, and the shaking device is set in motion. After a few minutes the reading of each burette is noted, and fermentation is allowed to continue for 6 hours, after which readings are again taken. The amount of carbon dioxide produced in 6 hours is greater in solutions containing aneurin than in the blank solution containing none, and the difference is proportional to the amount of aneurin present, all the other conditions of the experiment being kept constant. When aneurin in an unknown solution is to be assayed, one vessel is used for the blank test, another contains the solution to be tested, whilst the other four contain respectively 1, 5, 10 and 25γ (or other suitable amounts) of aneurin. By comparing the increase in the volume of carbon dioxide produced by the unknown solution with the increase given by the four standard solutions, the aneurin-content of the unknown solution is readily determined. The results were found to be reproducible with a fair degree of accuracy. The addition of aneurin did not bring about any regular increase in the dry weight of the yeast, nor an increase in the volume occupied by the yeast cells, but it did produce an increase in the number of yeast cells per ml. of solution. The absolute amount of carbon dioxide produced was dependent on the amount of yeast taken and on the amount of nicotinic acid present in solution, but neither of these two factors affected the amount of gas formed relative to the blank, nor, in consequence, the validity of the assay. The amount of glucose present was immaterial. Different results were obtained with a fresh and an old yeast, the latter being much more sensitive to aneurin than the former; the use of fresh cultures is therefore very important. The results were not invalidated by the presence of either acetaldehyde or pyruvic acid. Only three substances were found that stimulated carbon dioxide production under the conditions employed in the test. These were aneurin itself, co-carboxylase (1·4γ

was equivalent to 1γ of aneurin) and the pyrimidine component of aneurin. Nicotinic acid, nicotinamide, adermin (vitamin B_6), indoyl-acetic acid, inositol and sulphanilamide, were all tested and found to be inactive. It was not found possible to detect less than 0·1γ of aneurin. Similar results were obtained for the co-carboxylase-content of a solution by the fermentation test and by the modified thiochrome test of Westenbrink and Goudsmit (*Acta Neerland. Physiol.*, **1938**, 168), and the new method was successfully applied to the determination of aneurin and co-carboxylase in whole blood and blood extracts, flour and flour extract, and extracts of yeast, liver, kidney and other tissues. F. A. R.

Occurrence of Vitamin B_2 (Lactoflavin). Part III. Vitamin B_2 in Yeast and Yeast Extracts. J. Schormüller. (*Z. Unters. Lebensm.*, 1939, **77**, 459–466.)—The material used almost exclusively for the manufacture of yeast preparations is bottom yeast (*Saccharomyces cerevisiae*) from beer fermentation. The lactoflavin-content of a number of samples of commercial yeast and yeast preparations was investigated by extraction with aqueous acetone and colorimetric determination of the lumiflavin produced by irradiation of the extract according to the method already described (*Z. Unters. Lebensm.*, 1939, **77**, 1; Abst., ANALYST, 1939, 215). The results previously found by other workers indicated a range of 1·8 to 3·0 mg. of lactoflavin per 100 g. of dried substance, and the present experiments increased the upper limit of this range to about 4 mg. per 100 g. The experiments show that the process of manufacture of these preparations does not cause any loss of the vitamin activity of the yeast, and confirm the statement of Bing and Remp (*Proc. Soc. Exp. Biol. Med.*, 1934, **31**, 624), *viz.* that the vitamin-content of yeast is not affected by heating at 105° C. for 4 days, although its activity is destroyed by heating at 150° C. for 2 weeks. The results obtained by other workers from animal feeding experiments when calculated to lactoflavin-content (8γ of flavin being assumed equivalent to one rat unit) give figures from 4 to 5 times as high as those obtained by chemical methods, but, since it has been shown that the growth-promoting activity of lactoflavin is increased when the vitamin is associated with the other factors of the vitamin B complex, this discrepancy is to be expected. Experiments with yeast extracts gave figures varying from 4·01 to 6·96 mg. of lactoflavin per 100 g. of dried material, thus proving that, in the manufacture of extracts, treatment of yeast with superheated water under pressure causes no loss of vitamin B_2. As was found previously for liver (*Z. Unters. Lebensm.*, 1939, **77**, 346; Abst., ANALYST, 1939, 445), autolytic changes in yeast cause no measurable decrease in its vitamin-content (*cf.* Pett, *Biochem. J.*, 1935, **29**, 937). The following are examples of the amounts of lactoflavin (mg. per 100 g. of dried substance) found in medicinal preparations of yeast and yeast extract:—a lactoflavin glutathione product, 0·303; a concentrated vitamin B_1 preparation containing vitamin B_2 supplied in ampoules, 0·09; the same preparation in tablet form, 0·840; arsenical tablets containing yeast and yeast extract, 2·095; gastric tablets, 3·075; a liquid vitamin sedative preparation, 0·603. According to Euler and Adler (*Ark. Kem. Min. Geol.*, 1934, **11B**, No. 28; *Z. physiol. Chem.*, 1934, **226**, 88) in dried bottom yeast about 90 per cent. of the lactoflavin is in combination with colloid carriers. In order to determine how much of the flavin of yeast extracts is so combined, the sample (10 g.) was dissolved in 200 ml. of water and dialysed through cellophane into distilled water at 25° C. and at 3° C. It was found that in yeast extracts about 25 per cent., and in a yeast and malt extract about 35 per cent., of the total lactoflavin is not dialysable. The same result was obtained when the sample was first heated, with or without acidification, before dialysis, and it is concluded that the fraction of lactoflavin not passing through the membrane is not combined with a specific carrier as yellow enzyme, but is adsorbed by the high molecular constituents of the extract. This is confirmed by the fact that a large increase in the time of dialysis reduces the fraction retained by the membrane. An experiment in which a solution of pure lactoflavin was shaken with sufficient glycogen to form a solid glycogen phase showed that 9 per cent. of the flavin was adsorbed by the glycogen, and experiments with yeast gum as the adsorbing substance gave similar results. As both these substances occur in yeast extracts, they are probably the adsorbing agents. To determine the ratio of unesterified lactoflavin to lactoflavin-phosphoric acid in yeast extracts, a pure concentrate was prepared by adsorption upon and elution from fuller's earth and franconite (György *et al.*, *Z. physiol. Chem.*, **1934**, **223**, 27). Aliquot portions of this concentrate were extracted with benzyl alcohol (Emmerie, *Nature*, **1938**, **141**, 416; Euler and Adler, *ibid.*, 790) at *p*H 5·5 and in presence of 3 per cent. of sodium chloride, under which conditions only the unesterified flavin is extracted (Greene and Black, *J. Amer. Chem. Soc.*, **1937**, **59**, 1820), and it was found that 31·94 per cent. of the total flavin was in the free state. Since about 90 per cent. of the total lactoflavin of yeast is in the combined form, a portion of the lactoflavin-phosphoric acid is decomposed in the preparation of the extract. From a consideration of the results obtained it appears that about 70 to 100 g. of beer yeast, 50 to 80 g. of "vitamin yeast" or 40 to 50 g. of yeast extract suffice for the daily need of the human organism. The results of biological experiments indicate that about one-quarter of these amounts is sufficient. A. O. J.

Action of Light on Substances related to Ergosterol. G. A. D. Haslewood. (*Biochem. J.*, **1939**, **33**, 454–456.)—3-Hydroxy-Δ5:7-choladienic acid [$R = -CH(CH_3).CH_2.CH_2.COOH$] and its ammonium salt and 7-dehydrostigmasterol [$R = -CH(CH_3).CH:CH.CH(C_2H_5).CH(CH_3)_2$]



were irradiated, and the products were tested for vitamin D activity on rats in comparison with ergosterol [$R = -CH(CH_3).CH:CH.CH(CH_3).CH(CH_3)_2$] irradiated under exactly the same conditions. Whereas the latter contained about 4000 international units of vitamin D per mg., the other substances contained less than 10 units per mg., if any. F. A. R.

Bacteriological

Determination of Hydrogen Peroxide in Bacterial Cultures. E. R. Main and L. E. Shinn. (*J. Biol. Chem.*, 1939, **128**, 417–423.)—Samples of the culture, each measuring 1·0 ml., are placed in small tubes of equal diameter. To each are added 6 drops of potato extract, prepared as described below, and, immediately afterwards, 2 drops of a 10 per cent. solution of *o*-tolidine in glacial acetic acid. The tubes are allowed to stand until the maximum colour has developed. The time required for this is determined for each batch of potato extract by making comparisons with known amounts of peroxide over periods of about 8 minutes; it is usually 4 to 6 minutes. After standing for the necessary length of time the colours of the tubes are compared with those of appropriate standards in a comparator block, a blank, containing only sterile broth, potato extract and *o*-tolidine, being placed behind the standard solution to compensate for turbidity. The peroxide-content is calculated by reference to calibration curves made on the same day as the analyses. The potato extract is prepared from 120 g. of freshly ground potato by allowing it to stand overnight in an ice-box in about 130 ml. of a solution containing equal volumes of glycerin and phosphate buffer *p*H 7·2, the mixture being covered with a layer of mineral oil. The solution is decanted from the solid and, after being centrifuged, is ready for use. It retains its peroxidase activity for several days if a layer of mineral oil is floated on the surface. On the day it is to be used each extract is standardised with known amounts of peroxide. The permanent standards used for measuring the colour are made by suitably diluting a 1 per cent. aqueous solution of malachite green oxalate. When sealed in small tubes they keep indefinitely. Concentrations of 6 to 30γ of hydrogen peroxide per ml. can be estimated with an accuracy of 85 per cent. or more.
F. A. R.

Agricultural

Natural Decomposition of Bat Manure. J. Vorster Nel. (*Sci. Bull.* 155, *Dept. Agr. and Forestry*, S. Africa). The composition of so-called fresh bat manure varies very considerably, particularly with regard to the phosphorus-content, owing to contamination by lower and more decomposed layers. The phosphoric oxide content of fresh bat manure as collected from caves is usually higher than the original content, since the manure has a very low apparent sp.gr. so that even slight contamination from lower layers richer in P_2O_5 will increase the percentage considerably, but will not decrease the nitrogen-content proportionately. A sample of fairly fresh manure was divided into two parts, and from one, unbroken droppings were sorted out, (*a*), and the rest was discarded, while the other half, (*b*), was roughly screened to separate most of the stones. After grinding and sieving analysis showed (on the dry samples) total nitrogen (*a*) 10·20, (*b*) 8·12; total P_2O_5 (*a*) 4·15, (*b*) 7·15. The moisture-content of fresh bat manure in the air-dry condition is 7 to 8 per cent., and in caves under dry conditions about 11 to 14 per cent. The fresh manure contains about 10 per cent. of nitrogen on the moisture-free material, and 1 to 2 per cent. of P_2O_5, but accumulation, mostly as tricalcium phosphate, may bring the phosphate figure in time up to 40 per cent., although the percentage availability of P_2O_5 (2 per cent. citric solution) is higher in fresh samples. As ammonia is one of the first products of decomposition, and is followed by formation of nitrate, the older, more decomposed manure contains a large proportion of nitrate nitrogen. Nitrogen is lost either through drainage, as free ammonia or as free nitrogen, and the manure contains a very active microflora, causing rapid decomposition of organic matter. Decomposition may be so complete that even the less easily soluble ultimate mineral products, such as tricalcium phosphate, are removed, leaving a residue of silica, iron oxide and alumina, contaminated by sand and dust from the cave. The fresh manure contains enough organic matter with reducing properties to reduce all nitrates present to ammonia when digested with sulphuric acid for the determination of nitrogen by the Kjeldahl process. In old manure preliminary reduction of nitrate is necessary. Leaching accounts for the low proportion of sodium and potassium, the K_2O rarely exceeding 1 or 2 per cent. The original sulphur and calcium contents are about 1 and 0·25 per cent. respectively, but gypsum accumulates rapidly owing to external contamination with calcium. D. G. H.

Quantitative Extraction of Carotene from Grass. F. E. Moon. (*J. Agr. Sci.*, 1939, **29**, 295–301.)—Carotene in green vegetable material has usually been determined by a preliminary extraction of total carotenoids followed by the phase separation of carotene and xanthophyll. It is proposed to replace this by direct extraction with petroleum spirit in presence of alcohol. Hot alcoholic potash should not be used for the disintegration of leaf material and saponification of chlorophyll, as the resinous matter which is precipitated hinders subsequent extraction, but the saponification and extraction must be separate; saponification followed by extraction is considered preferable to the reverse order. Five g. of finely-chopped fresh grass, or 2 g. of dried grass meal, are boiled in a flask with reflux condenser for 1½ hours with 40 ml. of 20 per cent. potassium hydroxide solution, and the mixture is cooled and filtered, under reduced pressure, through moistened cotton-wool on a perforated disc. The residue is washed in a beaker four times with 25-ml. portions of industrial spirit and then with petroleum spirit (usually once) until this remains free from colour, all washings being poured through the filter. The precipitation which occurs through the interaction of the alkaline and alcoholic extracts is completed by shaking, and the precipitate is filtered off under reduced pressure and washed with petroleum spirit. The two extracts are shaken well together in a separating funnel; after separation into two layers the alcoholic solution is re-extracted three times with petroleum spirit. If the colour of the final extract is completely removed by 92 per cent. methyl alcohol the extraction of carotene is complete; otherwise, further extraction is required. After the combined petroleum spirit solutions have been repeatedly extracted with 92 per cent. methyl alcohol until this remains colour-free, the solution of carotene in petroleum spirit is washed with water and the pigment present may then be determined colorimetrically or otherwise. Results obtained by this method have been compared with those given by the methods of Ferguson and Bishop (ANALYST, 1936, **61**, 515) and Pyke (*J. Soc. Chem. Ind.*, 1936, **55**, 139T; Abst., ANALYST, 1936, 61, 497), the Lovibond tintometer and Ferguson's curve (ANALYST, 1935, **60**, 680) being used. The variance and standard error have been shown to be smaller than those for the other two methods, and it has been found that the results obtained are reproducible with considerable accuracy. E. B. D.

Substitution of Lactic Acid for Citric Acid in the Analysis of Basic Slag. A. Heiduschka and H. Wünsche. (*Chem.-Ztg.*, 1939, **63**, 317.)—In the course of experiments with a slag having a total phosphate-content equivalent to 13·2 per cent. of P_2O_5, Sirot and Joret have shown that 10·8 to 10·9 der cent. can be dissolved out in 30 minutes by means of a 2 per cent. solution of citric acid or by solutions of equivalent molecular strengths of lactic acid or malic acid; 7·4 to 7·6 per cent. by acetic acid or tartaric acid; 3·2 per cent. by oxalic acid, all of equimolecular strengths (*cf.* ANALYST, 1919, **44**, 180). Since citric acid and lactic acid behaved similarly and since the former was then the cheaper, these results have hitherto attracted little interest. The present authors have now repeated the experiments with 1, 2 and 3 per cent. solutions of these two acids and have shown that the difference between the two sets of results falls within the permissible limits of experimental error (*i.e.* 0·3 per cent., as phosphoric acid). This applied whether the period of agitation during extraction was 60 minutes with the 1 per cent. solution or 30 to 120 minutes with the 2 per cent. solution. Comparisons made on four samples of basic meal and with 2 per cent. solutions of the acids showed that the average difference between the results obtained with the two acids was 0·20 and 0·28 per cent. for the Lorentz and Popp (iron citrate) methods, respectively.

J. G.

Water

Analyses of Water of the Old Sulphur Well at Harrogate. (*The Harrogate Spa Medical J.*, 1939, **2**, 16.)—The Spa authorities are exhibiting in the Royal Pump Room a chart which shows in graphical form the saline and sulphur contents of the Old Sulphur Water as determined by various analysts from 1783 to the present time. The chart affords convincing evidence of the constancy of composition of this famous spring.

	Calculated in parts per 100,000	
	Total solids	Sulphur
Walker (1783)	1587	—
West (1823)	1464	—
Hunter (1830)	1451·4	—
Hofmann (1853)	1565·6	9·08
Muspratt (1867)	1584	9·62
Davis (1872)	1495·1	9·16
Thorpe (1875)	1495·9	9·33
Lowson (1912)	1508·5	9·43
Present day	1553·0	9·73

Organic

Separation of Oleic Acid from Saturated Acids and Linolic Acid, with Observations on the Preparation of Oleic Acid. P. J. Hartsuch. (*J. Amer. Chem. Soc.*, 1939, **61**, 1142–1144.)—A comparative study of various methods for the separation of saturated from unsaturated fatty acids showed that the Brown and Shinowara method (*J. Amer. Chem. Soc.*, 1937, **59**, 6; Abst., ANALYST, 1937, **62**, 325) was the most efficient. The separation of oleic from linolic acid was eventually made by an initial crystallisation of oleic acid from 10 vols. of acetone at −60° C. Owing to the separation of a considerable amount of linolic acid only 5 vols. of acetone were used for the last three crystallisations, which were carried out at −40° C. This gave a 10 per cent. increase in yield of precipitate without decreasing the effectiveness of the separation of the residual linolic acid. Still more of the remaining saturated acids were removed by a lead soap precipitation in 95 per cent. alcohol, with the use of three times as much lead acetate as would be required to react with the estimated amount of acids present. Distillation at about 1 mm. pressure in a still with electrically heated glass column 4 feet high, and with the still-head temperature controlled to give a reflux ratio between 5 : 1 and 10 : 1 was then carried out, and the 6th fraction was found to contain 97·8 per cent. of oleic acid, 1·0 of linolic and 1·2 per cent. of saturated acids. This is taken as probably representing the maximum purity obtainable by present methods.

D. G. H.

Elaidinisation of Linolic Acid. J. P. Kass and G. O. Burr. (*J. Amer. Chem. Soc.*, 1939, **61**, 1062–1066.)—Elaidinisation of linolic acid was carried out with nitrogen oxides, and most successfully with Poutet's solution, and with selenium. The solid crystalline product isolated had m.p. 28–29° C.; iodine value (Wijs), 178·3; thiocyanogen value, 90·0; neutralisation equivalent, 280. It gave a crystalline lead salt and was spectroscopically inactive. The calculated values for the formula $C_{18}H_{32}O_2$, are carbon 77·06, and hydrogen 11·50, and the figures found were 76·89 and 11·25, respectively. Equal parts of a liquid and solid tetrabromide (m.p. 78° C.) were found on bromination of the crystalline linolelaidic acid dissolved in ligroin. Partial alkaline oxidation with potassium permanganate resulted in the production of two sativic acids, with m.p. 146 and 122° C., respectively. In addition to the solid acid a liquid linolelaidic acid was produced in an impure form, together with conjugated by-products. Only liquid bromides could be obtained from this acid and partial oxidation again produced two sativic acids, with m.p. 126–127 and 156–158° C., respectively. It is suggested that linolic acid is either totally converted on elaidinisation or is present in the reaction mixture in too small quantities to be detected by bromination or partial oxidation, the removal of the solid isomer and conjugated by-products leaving a liquid fraction characterised by its ligroin-soluble bromide. D. G. H.

Use of Selenium in Kjeldahl Digestion of Leather for Nitrogen Determination. D. Williams. (*J. Amer. Leather Chem. Assoc.*, 1939, **34**, 261–263.)—The nitrogen in 30 samples of leathers of varying composition (from loaded to unloaded) was determined. Analyses were made in duplicate by the Official

A.L.C.A. method, and by that method with the addition of approximately 0·3 g. of selenium. Closer agreement between the duplicate determinations was obtained in the selenium digestions, and there was a saving of time in the digestion, only 1 hour being required instead of the usual 2¼ hours. Averages of all the determinations were as follows:—by the Official method: Nitrogen, 6·069, or as hide substance, 34·10 per cent., and by the modified method, 6·085, or as hide substance, 34·20 per cent. D. G. H.

Inorganic

Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Mercury, Tin, Cadmium and Zinc. H. H. Willard and G. M. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 269–274.)—*Mercury.*—The method depends on the precipitation of a white crystalline compound, which is insoluble in presence of sodium chloride, in accordance with the reaction

$$2(C_6H_5)_4As^{\cdot} + HgCl_4'' \rightarrow [(C_6H_5)_4As]_2HgCl_4.$$

The unused excess of the reagent is determined volumetrically; gravimetric determination is not possible because no suitable washing liquid could be found. The solution of mercury as mercuric nitrate is neutralised, if necessary, with sodium hydroxide solution and rendered slightly acid with hydrochloric acid. A limited excess of standard (0·01 to 0·03 M) tetraphenylarsonium chloride reagent is added, with constant stirring, and then enough sodium chloride to give a concentration of 1 to 2·5 M sodium chloride. The volume of the liquid should be 60 to 120 ml., depending on the quantity of mercury present. The precipitate is filtered off after 15 to 60 minutes and washed several times with saturated sodium chloride solution, and the filtrate and washings are titrated potentiometrically with standard iodine as previously described (*id.*, 1939, **11**, 186; Abst., ANALYST, 1939, 452); 1 ml. of 0·01 M reagent ≡ 1·0031 mg. of mercury. The error with amounts of mercury from 0·5 to 107 mg. in pure solutions is about ±0·06 mg. With the smaller amounts, a considerable excess of reagent is required and some hours are necessary for complete precipitation. Copper interferes, not with the precipitation, but with the titration of the filtrate, by liberating iodine; this may be avoided by adding sodium citrate and citric acid before the titration. In presence of ferric iron (up to 300 mg.) it is necessary to add sufficient syrupy phosphoric acid to discharge the yellow colour before precipitating the mercury, and then, prior to the titration, to add a further similar amount of phosphoric acid plus twice the weight of disodium phosphate. The interference of manganese and stannic ions can be overcome by the addition of tartrate to the solution before precipitation, but that of cadmium, zinc and bismuth, cannot be eliminated. Other interfering ions are tungstate, chromate, molybdate, chlorate, iodide, bromide, fluoride and thiocyanate.

Tin.—The method is similar to that for mercury. The compound precipitated is $[(C_6H_5)_4As]_2SnCl_6$. At the stage of precipitation the volume of solution should be 60 ml.; the concentration of sodium chloride 2·5 to 3 M for quantities of tin up to 30 mg., or 1·5 to 2 M for larger quantities; the acid concentration 0·4 to 1 M; 1 ml. of 0·01 M reagent ≡ 0·5935 mg. of tin. Phosphate, citrate, oxalate and fluoride prevent precipitation of tin; tartrate interferes only very slightly. The method is also affected by those substances which interfere with the determination of mercury.

Cadmium and Zinc.—These may be determined by methods similar to that for mercury. The compounds precipitated are also of analogous composition. The precipitation is quantitative in presence of a fairly high concentration of sodium chloride. The chlorocadmiate precipitate is considerably more soluble than the chloromercuriate compound, and the chlorozincate compound is still more soluble. Owing to the rather high solubility, these determinations are in general subject to more interferences than the others described above. S. G. C.

Separation and Determination of Copper and Nickel by Salicylaldoxime. L. P. Biefeld and D. E. Howe. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 251–253.)—Tests of the salicylaldoxime method showed that copper may be separated from nickel by precipitation with the reagent at *p*H 2·6–3·1. After precipitation of the copper, nickel may be quantitatively thrown down by adjusting the *p*H to 7·0–9·9. There was slight co-precipitation of nickel with the copper; thus with 500 mg. of nickel in the solution (250 ml.) only about 0·5 mg. of the nickel complex, $Ni(C_7H_6O_2N)_2$, was occluded when 25 mg. of copper were precipitated. The co-precipitation of iron with the copper was about 10 times as much as that of nickel. S. G. C.

Separation and Determination of Aluminium and Beryllium with Tannin. M. L. Nichols and J. M. Schempf. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 278–280). Moser and Niessner's method has been studied with regard to regulation of *p*H value, time of digestion and so on. The following process is recommended:—To the solution containing not more than 0·08 g. of alumina and beryllia together, 25 ml. of saturated ammonium acetate solution are added, and the *p*H is adjusted to 4·6 by the use of 6 *N* sulphuric acid and 1 : 1 ammonia. The solution is heated to boiling, tannin is added slowly (50 ml. of a 3 per cent. solution or at least 12 to 15 times the combined weight of alumina and beryllia present), and the liquid is digested on a steam-bath for 1 hour. After cooling to room temperature, the aluminium-tannin precipitate is filtered off on a coarse-textured paper, washed with a 5 per cent. solution of ammonium acetate containing a little tannin and adjusted to *p*H 4·6, ashed, ignited at 1200° C., and weighed. Beryllium is determined in the filtrate as in the method of Moser and Singer (*Monatsh.*, 1927, **48**, 673; ANALYST, 1928, **53**, 402). Good results were obtained in tests on mixtures. S. G. C.

Quantitative Determination of Calcium by means of Loretin. N. Schoorl. (*Pharm. Weekblad*, 1939, **76**, 620–625.)—Loretin (7-iodo-3-hydroxy quinoline-5-sulphonic acid) has been used as a qualitative reagent for calcium (*cf.* Van Zijp, ANALYST, 1932, **57**, 801), and under the following conditions it may be used quantitatively:—To 2·5 ml. of the solution to be tested (which should contain not more than 2 per cent. of calcium) are added 2·5 ml. of a buffer solution (*p*H 4) prepared by dissolving 80 ml. of 30 per cent. acetic acid and 10 g. of crystalline sodium acetate in water and diluting to 100 ml. The beaker is warmed on a water-bath, 25 ml. of the boiling reagent (see below) are introduced, and the mixture is shaken and left on the water-bath for 15 minutes. It is then allowed to cool slowly (important), and,

with small quantities (0·5 to 10 mg.) of calcium it is advisable to allow the cooling to take place in a closed box. The orange-red crystalline precipitate of monocalcium loretinate is separated on a sintered glass crucible (size 3G3), and washed in succession twice with the reagent, twice with 96 per cent. alcohol and once with acetone, 3 ml. of liquid being used for each wash (see below); the crystals are large and coarse, and are easily transferred to the filter. They are dried in air, and finally in a vacuum desiccator until constant in weight; they then have the composition $3[Ca(C_9H_4N.I.OH.SO_3)_2],10H_2O$, and the weight of calcium is obtained by dividing the weight of the precipitate by 20. This factor applies only when 10 to 40 mg. of calcium are present. With 4 to 16, 2 to 8 or 0·5 to 3 mg. of calcium, the volumes of original solution that should be used are 1·0, 0·5 and 0·2 ml.; buffer solution, 1·0, 1·5 and 0·2 ml.; reagent, 10, 5 and 2 ml., respectively. The corresponding weights of precipitate are then 80 to 320, 40 to 160 and 10 to 60 mg., respectively, and the appropriate factors are calculated accordingly. The reagent is prepared by shaking 8·8 g. of loretin with 200 ml. of water and adding 6·5 ml. of 4 *N* sodium hydroxide solution. The red-brown solution of sodium loretinate ("Meditren") is diluted to 250 ml. and filtered; if, in the course of time, fine crystals are deposited from the filtrate, the presence of traces of calcium as an impurity is indicated, and the solution should again be filtered. Metals other than sodium, potassium or magnesium must be absent. The precipitate, which is stable in air, may also be determined volumetrically by de Jong's method (*Pharm. Weekblad*, 1937, **74**, 608), each ml. of 0·1 *N* silver nitrate solution used being equivalent to 2 mg. of calcium. An important feature of the method is the amount and nature of the solvents used for washing the precipitate; thus, the solubilities of the precipitate in water, 50 and 96 per cent. alcohol, acetone and ether are 1 part in 1250, 800, 20,000, 50,000, and more than 200,000, respectively, at room-temperature.
J. G.

Catalytic Action of Selenium in the Kjeldahl Digestion Method. A. Sreenivasan and V. Sadasivan. (*Z. anal. Chem.*, 1939, **116**, 244–252.)—The mechanism of the catalytic action of selenium under the conditions of the Kjeldahl process was elucidated. By using selenium, selenious acid, and selenic acid, the authors have proved that selenious acid is the stable compound in hot strong sulphuric acid. If, however, mercuric oxide is present, selenious acid is rapidly and completely converted into selenic acid (under those conditions the stable form), and at a greater speed than that of the reduction of selenic into selenious acid by the organic matter. This explains the speed with which organic matter is destroyed by sulphuric acid in presence of mercuric oxide and selenium, the process requiring only one-third of the time taken when mercuric oxide is omitted. The form in which the selenium is added makes no difference. If no mercuric oxide is used, the selenium is wholly present as selenious acid at the conclusion of the operation; otherwise, only selenic acid will be found. It is concluded that the catalytic action of selenium in presence of mercuric oxide is due to the reaction $Se \rightarrow SeO_2 \rightleftharpoons SeO_3$. Without mercuric oxide the reversible reaction $Se \rightleftharpoons SeO_2$ occurs, resulting in more sluggish oxidation. The catalytic action of selenium is greatest during the initial stages of the digestion. W. R. S.

Determination of Fluorides in Wood Preservation Technology. I. Analysis of Solutions of Fluorides in Water. B. Ikert. (*Chem.-Ztg.*, 1939, **63**, 324.)—Existing methods (*e.g.* precipitation as calcium fluoride or titration with ferric chloride) are unsuitable, being too slow and easily upset by other substances (*e.g.* chromates, arsenates and dinitrophenol) likely to be present in the solutions concerned. The following method, which can be carried out in 35 to 40 minutes, is recommended when either a chromate or arsenate is present or when both are absent:—A mixture of 25 ml. of the solution to be tested (containing 0·1 to 0·25 g. of sodium fluoride), 5 ml. of a 3 per cent. solution of sodium silicate and 2 drops of methyl orange solution is neutralised with 10 per cent. hydrochloric acid. Two drops of the acid are then added in excess, and are followed by 1 g. of solid potassium chloride, and when this has dissolved 35 ml. of alcohol are added. After 20 minutes the precipitate of potassium fluosilicate is separated by filtration on a filter-paper or an asbestos-lined Gooch crucible, and washed with a 2 per cent. solution of potassium chloride in 50 per cent. alcohol until the total filtrate amounts to 100 ml.; filtration is more rapid on the Gooch crucible. The contents of the filter are then washed back into the original containing-vessel with 100 ml. of hot water, and the mixture is titrated with 0·1 *N* sodium hydroxide solution with phenolphthalein as indicator until a weak red colour is obtained; 0·3 ml. is added to the reading to allow for losses due to solubility of the precipitate. When approximately 0·2 g. of sodium fluoride was taken the resulting errors were +0·4, +0·8, and 0 to +0·3 in presence of 0·6 g. of potassium dichromate, 0·4 g. of sodium arsenate, and in absence of both salts, respectively. If chromates and arsenates are present together, they may combine under the influence of the alcohol to form a compound containing tervalent chromium, which is sparingly soluble and uses up some of the sodium hydroxide solution. The formation of this compound is accelerated by standing, by a high *p*H value, and by exposure to light, and the following precautions must therefore be taken. After neutralisation to methyl orange 0·3 ml. of the acid is added in excess, and, 15 minutes after the addition of the alcohol, another 0·3 ml. is added. The mixture is then immediately filtered. This procedure delays precipitation of the chromium compound, especially if exposure to sunlight is avoided. Duplicate tests on a solution containing 0·1357 g. of sodium fluoride, 0·125 g. of sodium arsenate, 0·1875 g. of potassium dichromate and 0·05 g. of dinitrophenol (*i.e.* corresponding with a commercial solution used for the impregnation of wood) gave results having an error of +0·2 and +0·4 per cent. If, however, large quantities of arsenates or chromates, or both, are present, they may be occluded by the precipitate and the results may be 1 per cent. high.

J. G.

New Specific Reaction for Nitric Acid and Nitrates. M. M. Pesez. (*J. Pharm. Chim.*, 1939, **29**, 460–465.)—With the exception of a few depending upon the formation of insoluble nitrates, the reactions used for the detection of nitrates are colour reactions which, although very sensitive are not specific, since they depend upon the oxidising action of the nitrate ion. The reaction of Janowski (*Ber.*, 1891, 971), in which *m*-dinitrobenzene is condensed with acetone in presence of alkali to form an intense violet colour, is adapted to the detection of nitric acid and its salts and, since the basis of the reaction is the formation of a nitro-compound, it is specific for the nitric ion. A few particles of the substance to be tested are treated in a test-tube with 12 drops of conc. sulphuric acid and 2 drops of benzene and, after thorough agitation, the tube is heated in a boiling water-bath for 3 minutes. If the substance to be tested is a liquid it is neutralised, evaporated to dryness in a glass capsule, and treated with sulphuric acid and benzene, the mixture being stirred well with a glass rod before being heated on the water-bath. When cold the reaction mixture is treated with 5 to 8 ml. of acetone followed by sufficient sodium hydroxide solution (about 20 per cent.) to render the mixture alkaline. If nitrate is present in the original substance an intense violet colour is formed. The colour changes very slowly to reddish-violet and finally to blood-red, the change being accelerated by the presence of water. If the nitration mixture is heated over a free flame instead of on the water-bath, trinitrobenzene may be formed, and the colour will then vary from reddish-violet to red. With the procedure described the test will detect 0·5 mg. of potassium nitrate in 1 ml. of solution. In presence of bromide or iodide the acetone is coloured by the liberated halogen, but the colour disappears when the sodium hydroxide is added, and the presence of these substances does not interfere with the test. Since nitrobenzene gives no colour with acetone and alkali, it may replace benzene in the test; it has the advantages that it is miscible with conc. sulphuric acid and that heating of the reaction mixture is unnecessary. If desired, a 10 per cent. solution of nitrobenzene in conc. sulphuric acid may be used as the reagent, and the mixture is allowed to stand for 2 or 3 minutes before the addition of acetone and alkali. Nitrous acid and nitrites do not answer to the test, and no compound has yet been found which simulates the action of the nitric ion. A. O. J.

Microchemical

Microscopic Examination of Polymorphous Compounds. (I) L. Kofler and E. Lindpaintner, (II) E. Lindpaintner. (*Mikrochem.*, 1938, **24**, 43–58; 1939, **27**, 21–41.)—(I) By using an electrically heated block, the melting point of individual crystals may be readily observed under the microscope. Transformation from one form to another can usually be best observed between crossed nicols. It is frequently possible to obtain individual crystals of the different modifications by micro-sublimation. Nipagin, veronal, atophan, morphine and a number of other substances sublime in different forms. Sublimation is carried out both at normal and reduced pressures. Benzil gives three modifications melting at 95°, 41·5° and 27° C., and 8-hydroxyquinoline gives four melting at 73·5°, 65°, 57–58°, and 38–39·5° C., respectively. Benzidine gives five modifications, four of which melt at 129°, 125°, 120·5–121° and 116·5–117° C., respectively, whilst the m.p. of the fifth cannot be determined. Ten photomicrographs are given. (II) Polymorphism is shown by the following substances:—Phenyl benzoate: three forms, melting at 69°, 56·5° and 51–52° C.; benzoyl-l-ecgonine: four forms, melting at 202–203°, 179–181°, 130–135° and 100–105° C.; quinizarin enantiotropic: two modifications —one orange, melting at 195° C., and the other, red, melting at 201° C.; chrysophanic acid: two forms, melting at 195° and 190° C.; coumarin: three forms, melting at 68·5°, 64·5° and 55° C.; gallic acid: two forms melting at 258–265° and 225–230° C.; hydroquinone: two forms, both melting at 172·5° C.; morphine hydrochloride: two forms, melting at 295–300° and 280–284° C.; nipagin: six forms, melting at 127°, 116°, 110°, 110°, 109° and 106° C.; *o*-nitrobenzaldehyde: two forms, melting at 42–42·5° and 39° C.; *m*-nitrobenzaldehyde: two forms, melting at 56–57° and about 51° C.; *p*-nitrobenzaldehyde: two forms, melting at 105° and 104–104·5° C.; phenanthraquinone: two forms, melting at 210–211° and 207° C.; veronal: four forms, melting at 190°, 183–190°, 183° and 176° C.; *m*-xylenol: two forms, melting at 62–63° and about 55° C. Details are given of methods of conversion. J. W. M.

Inorganic Spot Tests. F. Feigl. (*Rec. Trav. chim. Pays-Bas*, 1939, **58**, 471–480.)—(1) *Test for tungsten with diphenyline.*—The reagent is preferable to benzidine. A drop of a 1 per cent. solution of diphenyline hydrochloride in 2 *N* hydrochloric acid is added to a drop of the test solution; a turbidity indicates tungsten. For the smallest amounts comparison with the result of a blank test after 15 minutes is necessary; the limit of identification is then 6γ. (2) *Test for calcium with the osazone of dihydroxy tartaric acid.*—The test is not very selective, and salts other than those of ammonium and the alkali metals interfere. A white precipitate, visible against a dark background, is formed from solution as dilute as 1 in 5 million. The test has been found useful to distinguish between tap-water and distilled water. (3) *Test for sodium with zinc uranyl acetate.*—Limit of identification: 12·5γ of sodium on a black spot-plate, or 2·5γ by the greenish-yellow fluorescence produced when a drop of the solution on filter-paper is exposed for 1–4 minutes while still moist, to ultra-violet light. The reagent solution of zinc uranyl acetate is prepared by mixing a solution of 10 g. of uranyl acetate in 6 g. of 30 per cent. acetic acid, diluted with water to 50 ml., with a solution of 30 g. of zinc acetate in 3 g. of 30 per cent. acetic acid, diluted to 50 ml. A trace of sodium chloride is added to the warm mixture and, after 24 hours, any sodium zinc uranyl acetate is filtered off. (4) *Test for hydrazine with salicylaldehyde* (this test may also be applied quantitatively).—When a drop of the reagent is mixed with a drop of the test solution in a micro-test-tube a white precipitate is formed; limit of identification: 0·1γ of hydrazine. The reagent is prepared by boiling 5 g. of salicylaldehyde with 600 ml. of water and 20 ml. of 50 per cent. acetic acid until the oil has disappeared. The solution is filtered before use. (5) *Test for hydroxylamine with salicylaldehyde and copper acetate.*—The solutions must be mixed in the following order: A drop of the reagent solution (as above, Test 4) is mixed in a test-tube with a drop of the test solution and then with 2 drops of a filtered solution of 5 g. of copper acetate in 150 ml. of water and 1 or 2 ml. of 50 per cent. acetic acid. In presence of hydroxylamine a pale yellow precipitate or cloudiness is formed; limit of identification: 1γ. (6) *Test for hydrazoic acid by formation of silver or iron azide.*—A drop of the test solution is placed in a small tube closed with a glass stopper with a knob underneath on which hangs a drop of ferric chloride or silver nitrate solution. The acid is liberated on warming very slightly with 1 or 2 drops of dilute hydrochloric acid and, acting on the ferric chloride or silver nitrate, gives a red colour with the former or cloudiness with the latter. Limit of identification: 5γ of sodium azide. (7) *Test for ferrocyanide with uranyl acetate.*—A drop of *N* uranyl acetate solution is mixed on a spot-plate with the test solution. A brown precipitate is formed; limit of identification: 1γ. The test may also be carried out on filter-paper. (8) *Test for ferricyanide with benzidine.*—The test may be used in presence of ferrocyanide. The test solution is mixed with a drop of a saturated solution of benzidine in 2 *N* acetic acid; it is advisable to add also a drop of a 1 per cent. lead nitrate solution. A blue colour forms with as little as 5γ of potassium ferricyanide even in the presence of excess of ferrocyanide. (9) *Test for chlorate and periodate by formation of complex manganese phosphate.*—A drop of the test solution is mixed with a drop of a mixture of equal parts of saturated manganese sulphate solution and syrupy phosphoric acid and gently heated in a micro-crucible. A violet colour appears on cooling, in presence of chlorates or periodates. A pale colour may be intensified by adding a drop of a 1 per cent. alcoholic solution of diphenyl carbazide, when the limit of identification is 0·05γ of chlorate and 5·0γ of periodate. (10) *Test for sulphate with barium carbonate and phenolphthalein.*—A drop of the neutral test solution is mixed with a drop of a barium carbonate suspension and evaporated to dryness. On addition of a drop of an alcoholic solution of phenolphthalein a red colour indicates sulphates. It is advisable to ascertain if there is any interference when these tests are applied to the analysis of material containing a number of other ions. J. W. M.

Microcrystalline Reaction for Identifying Anthracene. G. Denigès. (*Bull. Trav. Soc. Pharm., Bordeaux,* 1939, 1; *J. Pharm. Belg.,* 1939, **21**, 308.)—A few particles of the product to be identified are placed on a glass slide and mixed with one drop of a solution of bromine in chloroform (preferably 5 per cent., never more than 10 per cent.). If anthracene is present, characteristic yellow needles of anthracene dibromide (m.p. 221° C.) are formed. The other cyclic hydrocarbons do not give this reaction. E. B. D.

Microcrystalloscopic Identification of Bromine in Chloroform Solution. G. Denigès. (*Bull. Trav. Soc. Pharm., Bordeaux,* 1939, 1; *J. Pharm. Belg.,* 1939, **21**, 308.)—Bromine, if present in aqueous solution, may be identified by the converse of the anthracene reaction (see preceding abstract). The solution is shaken well with chloroform and, after the mixture has stood, 1 ml. of the chloroform layer (which contains all the bromine) is transferred to a small conical flask, care being taken not to remove any water from the upper layer, and 2 droplets of a 1 per cent. solution of anthracene are added. If the solution becomes reddish-yellow, 1 or 2 drops are immediately evaporated and the crystals of anthracene dibromide formed are examined microscopically (×130 to 200); otherwise, the chloroform solution is concentrated before evaporation. E. B. D.

Electrolysis of Gold Solutions. M. G. Raeder and O. S. Kyllingstad. (*Mikrochem.,* 1939, **27**, 112–117.)—Gold chloride solutions containing 0·4 to 30γ of gold may be electrolysed quantitatively if they contain 3 to 5 drops 2 *N* potassium chloride solution. With the Pregl electrolysis apparatus deposition is complete after 20 minutes' boiling with a current density of 20–25 milliamps per sq.cm.; at room temperature when no stirring is used 4 hours is necessary. As anode a hard pencil lead may be used, but for a quantitative determination the gold is preferably precipitated upon sheets of assay lead, free from gold. The lead is then eliminated by the usual methods, and the residual bead of gold is measured micrometrically. J. W. M.

Physical Methods, Apparatus, etc.

Chelate Compounds as Flotation Reagents. C. C. De Witt and F. Von Batchelder. (*J. Amer. Chem. Soc.*, 1939, **61**, 1247–1249.)—The chelate compounds possess peculiar characteristics which have led to the investigation of their applicability as flotation reagents. Salicylaldoxime has been found effective for the separation of chalcocite, covellite, azurite, malachite and cuprite from siliceous gangue materials. The siliceous gangue material (50 g.) was placed in the flotation cell (enamelled cast-iron type) with 0·5 g. of the ore, 200 ml. of water were added and the stirrer was started (1750 r.p.m.). The aqueous solution of the required strength of oxime was then added, and was followed, after 3 minutes, by 2·5 mg. of the frothing agent (1 vol. of pine oil in 9 vols. of ethanol). The froth was collected over a period of 3 minutes, filtered on a Gooch crucible, dried and weighed, and its copper-content was determined. The residual gangue was also analysed to detect any possible errors in the previous analyses of the ores. Maximum recoveries of copper varied from 89·7 per cent. for cuprite (8 lb. of oxime per ton) to 97·7 per cent. for malachite (2·0 lbs. of oxime). It was found that replacement of the *ortho*-hydroxyl group of salicylaldoxime by a methoxy group gave a methoxylbenzaldoxime which was of no use as a flotation reagent. D. G. H.

Normal Oximes as Flotation Reagents. C. C. De Witt and F. Von Batchelder. (*J. Amer. Chem. Soc.*, 1939, **61**, 1250.)—All the normal oximes, including octyl oxime, were tested qualitatively as flotation reagents, but heptaldoxime and octaldoxime were the only ones that proved suitable for the separation of oxide, carbonate and sulphide ores of copper from siliceous gangue material. The flotation experiments were carried out as before (see above). Maximum recoveries of copper per cent. were as follows for (*a*) *n*-heptaldoxime and (*b*) *n*-octaldoxime:—chalcocite (*a*) 98·7 (0·4 lb. of oxime per ton), (*b*) 97·2 (2 lb.); malachite, (*a*) 89·6 (2 lb.), (*b*) 92·4 (2 lb.); covellite, (*a*) 95·4 (2 lb.), (*b*) 96·5 (2 lb.); azurite, (*a*) 85·5 (2 lb.), (*b*) 87·0 (2 lb.); cuprite, (*a*) 96·8 (4 lb.), and (*b*) 96·4 (2 lb.). D. G. H.

Viscometric Method for the Characterisation of Soluble Starch. W. A. Richardson. (*Chem. and Ind.*, 1939, **58**, 464–465.)—Since "soluble starch" is not an individual substance or even a mixture having constant and reproducible properties, and since the chemical reagents used in its manufacture vary considerably, it is not possible to evaluate such products by chemical methods. As with cellulose, evaluations have been made by viscometric methods (see Gallay and Bell, *Canad. J. Res.*, 1936, **14B**, 360), but difficulty has been experienced in finding a suitable solvent, because the lightly-modified starches swell before dissolving, and they must then be dispersed by the action of heat, and this results in further modification. Moreover, solutions of such starches in water are unstable and their viscosities are affected by the presence of electrolytes, whilst the viscosities of solutions in alkali do not remain constant, and are sensitive to mechanical treatment and to the presence of impurities. The solvent now recommended is a solution of calcium thiocyanate. A suspension of starch in cold water is poured into sufficient boiling water to produce a 2·5 per cent. solution or paste, which is then heated for about 1 minute and cooled. It is then passed through an homogeniser, and the concentration is determined by means of the dichromate method of Richardson, Higginbotham and Farrow (*J. Text. Inst.*, 1936, **27**, 131T). To 10 ml. of this solution are added 15 ml. of a 50 per cent. solution of calcium thiocyanate, a control solution consisting of 30 g. of calcium thiocyanate in 100 ml. of water being also prepared. The viscosity of 10 ml. of each solution is then measured in separate U-tube viscometers (*cf.* Higginbotham and Richardson, *J. Soc. Chem. Ind.*, 1938, **57**, 234), which are placed in a water-bath at 25° ± 5° C., and if n is the viscosity of the starch solution relative to that of the control solution, and c is the concentration of starch in g. per 100 ml., then the quantity $(\log n)/c$ is known as the "thiocyanate viscosity" (*TV*). It has been found that with potato, sago and maize starches, which have been modified in solution by means of hot dilute acids and then neutralised, the degree of modification is accurately measured by the reducing power (*R*) as determined by the method of Richardson, Higginbotham and Farrow (*loc. cit.*); moreover, since for such starches *TV* is a measure of *R*, *TV* may also be used as a satisfactory index of the degree of modification. With other starches (*e.g.* those that have been modified by oxidation, or by treatment in a granular condition with acids, followed by washing, which removes some of the reducing substances), *TV* is to be preferred to *R* as an index of the extent of modification. Tabular data show that with unmodified starches and starches that have been lightly modified by acid, the thiocyanate viscosity is very sensitive to mechanical treatment and therefore varies with the efficiency and duration of the homogenising process; since, however, this effect decreases as the degree of modification increases, when *R* exceeds a certain value (namely 40) homogenisation is unnecessary. Modification by oxidation, however, may result in a lower value of *R* than modification to the same extent, but by an acid process, and it may not be necessary to homogenise even when *R* is less than 40; values of *R* of from 5 to 160 are recorded for commercial soluble starches which have been modified by different methods and to different extents. When c is between 0·6 and 1·0 per cent. *TV* is independent of c, and so long as c is known accurately it is unnecessary to adjust it to a given value. *TV* is also independent of the concentration of sodium sulphate (up to 17·5 per cent. on the weight of starch) or of sodium chloride within the range of concentrations such as are likely to occur in commercial soluble starches. *TV* is slightly lower at 60° C. than at 25° C., but the difference rarely exceeds 5 per cent., and in any event the use of a control solution in the same thermostat eliminates any errors from this source. The thiocyanate solutions of acid-modified starches are unchanged in appearance and *TV* after 36 days at room-temperature, but the *TV* of certain oxidised starches falls slowly by about 0·02 in 8 to 36 days. J. G.

Electrolytic Polishing of Tin and its Application to Micrographic Examination. P. A. Jacquet. (*Intl. Tin Res. Development Council*, Pubn. No. 90, Feb., 1939.)—The usual technique for polishing metals for microscopical examination is unreliable for a soft metal such as tin, which is easily deformed by mechanical treatment and shows recrystallisation phenomena even at room temperature (*cf.* Taffs, *id.*, Pubn. No. 47, 1936). Polishing by electrolytic methods, *i.e.* by anodic treatment under controlled conditions (*cf.* Jacquet, *Compt. rend.*, 1935, **201**, 1473; 1936, **202**, 402; 1937, **205**, 1232; Elmore, *Phys. Rev.*, 1938, **53**, 757) is therefore preferable; in addition, this method stresses the crystal boundaries and produces characteristic corrosion figures within the crystals. The electrolytic cell is a beaker (250 or 500 ml.) in which are immersed vertically and a few cm. apart the specimens to be polished (the surface of which should not exceed 10 sq.cm.) and a piece of tinfoil having a surface larger than that of the sample. These form the anode and cathode, respectively, and are connected in series with a source of D.C. (25 to 40 volts), an ammeter, a variable resistance (about 150 ohms) and a switch. The beaker, which is immersed in a vessel of cold water, also contains a stirrer, a thermometer, and a solution prepared by pouring 806 ml. of 98 per cent. acetic anhydride very slowly into 194 ml. of perchloric acid (sp.gr. 1·61), the containing vessel being held under running water so as to avoid any rise in temperature. The electrical contact with the specimen should be so arranged that no foreign metal is immersed in the solution, *e.g.* by the use of a pinch-clamp above the level of the liquid. If, however, it is desired to polish the whole surface of the specimen, a piece of tin wire must be inserted through a hole in it; this arrangement has the disadvantage that mechanical deformation may result. Any oxide layer on the specimen (due to thermal treatment) is first removed, and the temperature is adjusted to 15° to 22° C. and the current-density to 9 to 15 amp. per sq.dm. (calculated on the total area of the anode); these conditions should be maintained during electrolysis, the latter by adjustment of the resistance, and they correspond with the dissolution of about 3 mg. of tin per sq.cm. or a layer 0·005 mm. thick per minute. When the polishing is complete (as indicated by the bright appearance of the specimen) the anode is removed quickly (without breaking the circuit), washed rapidly in succession under running tap-water (for 2 minutes), distilled water, alcohol and ether, and finally dried in a stream of compressed air which has been filtered through cotton-wool. If the specimen is complicated in shape, two cathodes, each placed 4 cm. away from it, are desirable. So long as the solution is stored in a glass-stoppered bottle and away from access of moisture, it may be used continuously until it is no longer possible to obtain a brightly polished surface; the deepening of the colour of the solution does not impair it. Etching or corrosion figures, the shape and orientation of which are characteristic of the crystals present, may be obtained by the use of a solution prepared from 130 ml. of glacial acetic acid and 50 ml. of the perchloric acid. The voltage should then be 15 volts D.C., and the current-density 3 to 6 amp. per sq.dm. of total anode area when the specimen is immersed in the liquid, as well as subsequently; this is ensured by making the necessary adjustments during a preliminary experiment on a similar specimen of tin; if necessary, an insulating varnish may be applied to the portions of the specimen which it is not desired to treat. Cooling and stirring are unnecessary, and the duration of electrolysis varies from 100 to 200 seconds according to the effects desired. The polished and well-dried specimen should be immersed with the current already switched on. Microscopical examination after electrolytic polishing reveals only the boundaries of the individual crystals. The etching process, however, enables small crystals (which are etched more rapidly), twins and other peculiarities to be seen. Various applications of the method are described and illustrated by 22 photomicrographs (magnifications up to ×1850). It is demonstrated that Chempur tin (99·99 per cent. Sn) when cast and unannealed, has a heterogeneous structure which persists after rolling-down from 1·5 to 0·36 cm. ("rolling-ratio," 76 per cent.), and disappears only after prolonged annealing (*e.g.* for 384 hours at 200° C.). Since tin of 99·9998 per cent. purity does not show these heterogeneities, these are ascribed to the presence of metallic impurities; the impure metals probably crystallise separately after the formation of a "skeleton" of pure tin. The changes in structure that occur in tin (99·99 per cent.) and tin-antimony alloys (0·5 to 3 per cent. Sb) when rubbed with an abrasive (*e.g.* fine emery paper, grade 06) have also been studied, the specimens having previously been rendered homogeneous, by prolonged thermal treatment at 200° C. It is shown that under these conditions the layer of tin so deformed is 0·20 to 0·25 mm. thick, and that it has acquired a new structure consisting partly of small crystals formed by recrystallisation at or slightly above room temperature, and partly of needle-shaped structures ("cold-working figures"). With the alloys a zone of anomalous structure is also produced, but as a rule only cold-working effects (orientated in the direction of abrasion) are observed without the recrystallisation effects. Annealing for 15 minutes at 200° C. is sufficient to remove these figures, and to re-form the normal type of crystals. It is claimed that such effects could not be investigated by the usual methods of polishing and etching, as these would in themselves induce changes in the structure of the specimen. J. G.

Reviews

TEXTBOOK OF ORGANIC CHEMISTRY. By GEORGE HOLMES RICHTER. Pp. viii + 711. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 20s. net.

In the preface it is stated that this textbook is directed specifically to that large body of ambitious students who wish to study organic chemistry and gain more than a superficial knowledge of the subject. With this in view the material is arranged so that emphasis falls on the fundamental principles of the science, namely, nomenclature, synthesis, reactions and properties. The aim of the book is to help the first-year student of organic chemistry to understand the subject. The work does not pretend to be an advanced exposition and does not therefore over-emphasise the importance of the electron theory of valency, as a comprehensive study of this subject would involve an intimate knowledge of higher mathematics and physics.

The book is divided into thirty-two chapters, the first twenty-one (456 pages) being devoted to the aliphatic series. Then follow nine chapters (191 pages) dealing with the aromatic series. The last two chapters (33 pages) give a brief description of the heterocyclic series, including the more important members of the alkaloid group. Each chapter concludes with a set of problems based on the work dealt with. The index occupies thirty-one pages.

The author has done his work well and has given to the student a valuable and concise treatise on the subject, which should be of use to him long after he has completed his first year. The book is well produced and is practically free from errors and misprints. The numerous diagrams and tables are represented very clearly. The reviewer has no hesitation in recommending the work to all students and teachers of organic chemistry. R. H. SLATER

LEHRBUCH DER ORGANISCH-CHEMISCHEN METHODIK, I BAND: ANALYSE UND KONSTITUTIONS-ERMITTLUNG ORGANISCHER VERBINDUNGEN. 6 ED. Dr. HANS MEYER. Vienna: Julius Springer. Price, stitched RM,57; bound RM.59.70.

This volume of 886 pages contains an extraordinarily large amount of information. The descriptions of what may be called the laboratory arts of organic chemistry—the choice of solvents for crystallisations, the drying of solvents and other practical details of manipulation—are of great utility and are given in more detail than in any other book with which the reviewer is acquainted.

Following a detailed account (pp. 115–208) of the quantitative analysis of organic compounds containing the usual elements, there is a very useful collection (pp. 210–268) of the various methods available for the estimation of other elements, from aluminium to zirconium, which may occur in organic compounds.

The main portion of the work (pp. 361–816) gives a detailed and well documented account of the methods for the characterisation of the more important groups and radicals and for their estimation: new methods are well represented and the references to quite recent literature are very numerous.

A chapter of twelve pages gives an account of the recently developed methods of separation by chromatographic adsorption.

It is unfortunate that the cost of this useful work should be so high.

J. KENYON

THE STRUCTURE AND COMPOSITION OF FOODS. Vol. IV. By ANDREW L. WINTON and KATE BARBER WINTON. Pp. xxxiii + 580. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1939. Price 45s. net.

This volume, the fourth of the series, opens with addenda to Volumes II and III, the greater portion of which is concerned with vitamins. It is an interesting commentary on the times that every book published on the science of food must now detail the latest chemical data dealing with the structure of the vitamin molecules. Why, the reviewer fails to see. The latest theories regarding the molecular structure of many of the major constituents of the foods mentioned are not recorded. One can only assume that the chemistry of vitamins is of scientific "news value"! The addenda are interesting but not important.

The body of the book is divided into four parts.

Part I. Saccharine Products.—The sections dealing with cane and beet sugars, maple sugar, honey, glucose and caramel give a good resumé of the preparation and chemistry of these products, including a large number of references, many useful, but some out of date. Nevertheless, there is little information given concerning the various grades of white and brown sugars encountered in commerce in England.

The inclusion of sections on sugars obtained from less common sources (palms, for example) is unusual and useful.

Part II. Alkaloidal Products.—In this section there is much information gathered together concerning products other than the main products, tea, coffee and cocoa. The clearest passages are those concerned with the macro- and micro-structure of the different plant products, a subject upon which the authors are recognised authorities. The lack of critical selection of data—noticeable throughout the book—is very obvious here, for many methods of analysis and results of analyses varying in age from 20 to 40 years are quoted. References to literature, however, are quite representative of modern thought. One might regret the lack of references to the work of Knapp on cacao fermentation. The reviewer gathers that the authors are not really conversant with the subject on which they write, otherwise such phrases as the following would not appear. "The seeds" of *Theobroma cacao*, "freed from the adhering pulp, are sun-dried either immediately or after being subjected to a fermentation, continuing for several days, that improves the flavor" (p. 114). "Some manufacturers also remove the minute radicles known in the trade as 'germs.' " (p. 114). "The gain in fiber" on roasting " . . . is doubtless due to the formation of charcoal . . ." (p. 120). They also quote seriously a formula attributed to Elsson for a substitute for cacao butter, consisting of a hydrogenated fat, lanoline and yellow wax (p. 131).

Part III. Spices and Extracts.—The characteristics chiefly praised in the review of the first volume of the series are perhaps best demonstrated in this part, for the macroscopic and microscopic descriptions are clearly stated and the drawings well chosen. The authors naturally deal with the subject-matter from the American aspect. Presumably, for example, the adulteration of dried mint by ailanthus leaves is never practised in the States, since this possibility is not mentioned in the text. Nevertheless, this is by far the best section of the book.

Part IV. Leaven.—The idea of this may be gathered from the following:—"Yeast may be defined as *biological* leaven and sodium bicarbonate and baking powder containing it as *chemical leaven*" (p. 465).

As with the vitamins, this section appears to be out of balance with the specialised treatment of the enzyme and co-enzyme systems in yeast. Certain phrases appear to suggest an incomplete appreciation of the implications, as, for example, "albumin changes little up to liquefaction, the increase in soluble nitrogen being gradual" (p. 469). "Neuberg . . . , by adjusting the volume of the medium to the dry weight of dried yeast, was able to stop the fermentation of hexose diphosphate at the pyruvic acid stage" (p. 488). The reviewer does not understand why the formula of lactic acid is expressed in the form $C_3H_6O_3 + C_3H_6O_3$ (p. 489). The following quotation is somewhat amusing. "As compared with yeast, it (baking powder) is a time saver, and time in the Western World is money" (p. 524). Another curious statement is that practically all brands of baking powder contain "starch or less often flour, added to improve the keeping power and to standardise the carbon dioxide liberated, which incidentally adds somewhat to the nutritive value" (p. 525). Notwithstanding these criticisms, this part, shorn of certain irresponsible comments and ambiguities, represents a useful contribution to food literature.

In conclusion, the reviewer would class this volume between the good first two volumes and the more unsatisfactory third volume. L. H. LAMPITT

PHYSICAL CONSTANTS OF HYDROCARBONS. Vol. I. By GUSTAV EGLOFF. Pp. 403. New York: Reinhold Publishing Corporation; London: Chapman & Hall. 1939. Price 45s.

This volume, the first of a projected series of four, has as its sub-title "Paraffins, Olefines, Acetylenes and Other Aliphatic Hydrocarbons." Subsequently, the cyclic and aromatic series will be dealt with, and the final volume will review the relationships suggested by the data thus collected, between members of each homologous series, and between one homologous series and another.

The present volume aims at recording physical constants for every open-chain hydrocarbon isolated and identified, whether from vegetable, animal or mineral sources, up to November, 1938. Standard tables and reference-books have been laid under contribution; but, owing to the great and increasing activity in this field within the last few years, the major part of the material has been collected from individual papers and from private communications, and has not previously been brought together. It is not easy to estimate the degree of completeness with which the task has been accomplished. Random sampling suggests that any omissions which may occur must be very few and trifling; for example, although Whitmore and Southgate's publication on tetramethylpentane (*J. Amer. Chem. Soc.*, November, 1938) has apparently not been read, a private communication from the same authors is quoted, giving all the published information except the refractive index.

The constants generally given are melting-point, boiling-point, specific gravity and refractive index. When a number of determinations of a single constant are available, a preferred figure has been evaluated from these, each being weighted in accordance with its probable error where stated, and otherwise in accordance with the author's estimate of its accuracy, based on the technique described in the original paper for the preparation and examination of the compound concerned. Readings for a variety of temperatures and pressures are given, if available; and, where the range of values justifies it, coefficients are deduced for calculating constants at other temperatures and pressures as required. The Geneva nomenclature, applied in a methodical way which is carefully explained and which avoids the need of an index, is used throughout, and supplemented by a graphic representation of each carbon-skeleton involved. When the only published data refer to mixtures of isomers (*e.g.* many cases of geometrical isomerism in the olefine series, or paraffins of high molecular weight where the number of isomers may approach millions) the fact is stated.

The work, when completed, cannot fail to be of great value in both pure and applied chemistry. To the pure chemist it opens much ground, not hitherto surveyed, on which to base correlations between properties and molecular structure. To many industrial chemists it will be an invaluable work of reference. The advances of recent years in fuel and lubricating oil technology have, to a considerable extent, revealed the dependence of the industrial usefulness of different oils upon the presence and proportion of various specific components; while the synthesis of alcohols, ketones and other solvents from cracked hydrocarbons has also been greatly developed. The identification of individual hydrocarbons must thus be of increasing importance to workers in these fields. The survey promised in the fourth volume should be welcomed by chemists, as providing both a basis for inductions of theoretical significance and an instrument enabling the technologist to forecast properties which would make it desirable to isolate or synthesise hydrocarbons that might otherwise have escaped attention. E. G. KELLETT

PLANT BIOLOGY. By H. GODWIN, M.A., Ph.D. Pp. x + 308. 3rd Edition. Cambridge: The University Press. 1938. Price 7s. 6d.

Since the previous edition was published six years ago, *Plant Biology* has been revised and enlarged, and there is little doubt that the book has been considerably improved by the additions made. The most important of these are the entirely new chapters on "The Fern Plant" and "The Flower and the Seed," so that the book now tells the complete story of the biology of plant life from the one-celled organism at one end of the evolutionary scale to the flowering-plant at the other. The story is told with the medical student, for whose especial benefit it is primarily intended, very definitely in mind, and as the title implies, the book is much more a text-book of biology than of botany. Moreover, the examples that the author takes to illustrate his theme are chosen with a view to the usefulness, in the student's later work, of the knowledge thus gained; thus more than the usual amount of space is devoted to a discussion of the biology of bacteria and fungi.

The book should prove of great value to those whose work lies on the borderland of chemistry and the biological sciences, and it can also be warmly recommended to others who may be less immediately concerned with plants, as a very clear and interesting account of how plants function. F. A. ROBINSON

THE PRINCIPLES OF ELECTROCHEMISTRY. By DUNCAN A. MACINNES. Pp. 478. New York: Reinhold Publishing Corporation; London: Chapman & Hall. 1939. Price 30s. net.

In this volume the author has endeavoured to present a unified treatment of the principles of electrochemistry on the basis of the concept of free energy as expounded by Gibbs. He traces the relationship between chemical potential and the activity of ions and then proceeds to discuss the Debye–Hückel Theory of Strong Electrolytes in regard to the assistance which it gives in the calculation of mean ionic activities from the E.M.F.'s of appropriate cells. No serious difficulties are encountered until "cells with liquid junctions" are considered, when the author is careful to point out, though in the opinion of the reviewer not with sufficient emphasis, that in order to apply thermodynamic equations to these cells, it is necessary to know the *ionic activity of a single ion*, for the determination of which no method has yet been devised. In consequence, non-thermodynamic assumptions are introduced. The author is careful to indicate when resort is made to these assumptions. This constitutes a very serious and, at the present, an insurmountable difficulty in the application of the Activity Theory to solutions of electrolytes when being investigated by means of this type of cell. Incidentally, cells of this type find the most practical application in the analytical laboratory. The difficulty is encountered in the electrometric methods of determining *p*H and it is also involved in the computation of the potentials of standard half-elements, *e.g.* the normal calomel electrode.

The treatment accorded in the book to *p*H determination, oxidation-reduction potentials and potentiometric titrations has a distinct bias towards the mathematical theory. From the standpoint of the experimentalist, the chapters on these subjects are too inadequate to be of much service.

A comparatively small part of the book is devoted to the Debye–Hückel–Onsager theory and its use in the interpretation of the electrical conductivity of aqueous and non-aqueous solutions. A very brief survey of conductometric titrations follows.

The remaining chapters are of a rather miscellaneous character. They deal with subjects such as Structure of Organic Acids and Bases in relation to their Ionisation Constants, Dielectric Constants, Electrokinetic Phenomena, Passivity and Overvoltage. The treatment of these subjects is incomplete, cursory and disjointed. It is surprising that the general principles underlying electrolytic preparations and depositions find no place, whereas overvoltage and passivity are especially singled out for discussion. In connection with overvoltage there is not even a reference to Glasstone's work.

It should have been mentioned that in the preliminary chapters, Dr. MacInnes discusses the Classical Theory of Arrhenius and also provides a lengthy chapter on Electrical Transference. It is with his investigations on this subject that Dr. MacInnes' name is largely associated.

The theoretical development of the subject-matter throughout the main part of the volume certainly makes the treatise of considerable importance to advanced students and to post-graduates. It is hardly likely to be of much help to the elementary student, for in order to follow the subject intelligently as discussed in the book, it is essential that the student should have previously obtained a sound grasp of the more advanced principles of thermodynamics. The author's aim appears to have been to write a connected mathematical exposition of electrochemistry from the standpoint of thermodynamics and modern theory, and in this respect he has undoubtedly succeeded. It is felt, however, that this method of attack has been rendered possible by the omission of much that would be valuable from the practical point of view.

The book is exceedingly well produced, but its price is perhaps a little high.

H. T. S. BRITTON

Annual Reports on the Progress of Applied Chemistry. 1938—Vol. XXIII. Issued by the Society of Chemical Industry. Pp. 856. Price to members, 7s. 6d.; to non-members, 12s. 6d.

The present volume has forty pages more than the last, and two new chapters appear, their titles being "Plastics" and "Explosives." Some of the twenty-six chapters have slightly modified titles, but their main subject-matter is the same as last year. The writing of each chapter and the reading of the very great number of papers to which reference is made, is a laborious task, and it is therefore not surprising to find the names of a number of new contributors in the table of contents.

Though most of us are specialists in one or two branches of our science with which the present work deals, few among us do not find it profitable to scan the progress made in other branches; such a book as this makes it much easier and more agreeable than the actual searching among hundreds of recent papers. Indeed, as almost everyone must know, one of the main purposes of these Reports is to assist the reader easily to make a choice of the papers most likely to interest him.

The literary style and all the other attributes of the volume under review are well up to the excellent standard of its predecessors. As an indication of the extent of the ground covered it may be mentioned that the name-index has some 4500 entries and the subject-index about 2900, the former being approximately the same as last year, the latter about 200 more. A count of the number of original papers referred to in the text gave a figure of over 4000. A careful search for errors of expression, punctuation and printing, revealed none of consequence and very few in actual number.

It is fascinating to follow in certain sections how the main interest shifts from year to year; in the section dealing with fine chemicals and medicinal substances, to give only one instance, formerly it was anti-malarials, then hypnotics—the veronal derivatives and so forth—and to-day it is drugs of the sulphanilamide class and chemotherapy in general.

The total benefit to mankind represented by the progress made in chemistry even in one year must be very great; in this benefit even animals and plants share—as witness the advances made in our knowledge of parasiticides and fungicides, their uses and mode of application. Of all this progress adequate notice is taken here.

At the modest price charged for the book it is safe to say that its issue represents more a labour of love than a source of profit. To those whose work is in the field of applied chemistry it will prove indispensable, and even to the "pure" chemist it may be recommended as being more than likely to provide fruitful ideas. This is borne out by the fact that some of the research in applied chemistry receives mention in the companion volume on pure chemistry issued by the Chemical Society.

F. W. Edwards

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4. SEP. 1939

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE tenth Summer Meeting was held at the Prince of Wales Hotel, Scarborough, from June 9th to 12th. The attendance, which included many ladies, was sixty.

The Chairman (Professor T. P. Hilditch) presided, and among those present were the following:—President (Professor W. H. Roberts); Past-Presidents: Dr. Bernard Dyer with Mrs. Dyer, Mr. J. Evans, Mr. E. Hinks with Mrs. Hinks, and Dr. G. Roche Lynch with Miss Roche Lynch; Honorary Secretary (Mr. L. Eynon); Honorary Treasurer (Dr. E. B. Hughes with Mrs. Hughes); Scottish Section, Honorary Secretary (Mr. J. B. McKean); Miss Bradford; Mr. R. C. Chirnside; Dr. H. E. Cox; Mr. F. W. Edwards and Mrs. Edwards; Mr. E. M. Hawkins; Mr. F. G. H. Tate and Mrs. Tate; Scottish Section: Mr. A. R. Jamieson.

The Chairman gave a welcome to all members, particularly those from the South and from Scotland, and also referred to the great loss sustained by the Society since the last Summer Meeting by the death of Dr. J. T. Dunn and Mr. E. R. Bolton.

On Saturday morning a paper was read by G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D., F.I.C., on "Lead in Food." A discussion followed the paper, and a resolution of thanks, proposed by Mr. S. E. Melling and seconded by Mr. A. R. Jamieson, was unanimously passed to Dr. Monier-Williams for contributing the paper.

A resolution expressing the greetings of the Section and declaring its loyalty to the Council and the Parent Society was proposed by Mr. J. G. Sherratt, seconded by Mr. F. Robertson Dodd, and was passed unanimously.

On Sunday afternoon a motor run was made over the moors towards Whitby, and tea was taken at the Goathland Hydro.

Grateful acknowledgment is made by the Honorary Secretary, Mr. J. R. Stubbs, to the following for their services in carrying out the arrangements:—Mr. W. G. Carey, Mr. A. Lees, Mr. T. W. Lovett, and Mr. F. J. Smith.

Biological Standardisation

By Sir HENRY DALE, C.B.E., M.D., F.R.S.

(*Address given at the Annual General Meeting, March 3rd,* 1939)

THERE are many important medicinal substances and preparations for which the ordinary chemical and physical methods of analysis are unable to give the data required to standardise them. Many of them have powerful, definite and therapeutically important activities, making them directly dangerous in some cases if they are given in excess. It is accordingly a matter of practical urgency that preparations of such substances should be standardised to a constant strength, specified within narrow limits, or should have their potency indicated in some clear and accepted notation. The latter is much the more desirable aim. It enables dosage to be given in real equivalents in practical medicine, and, what is even more important, it provides a common basis for the expression and record of the results of research, which has often been greatly hampered and retarded by the lack of it. The principles responsible, in such cases, for the specific actions are as yet unknown, or, if known, cannot for one reason or another be measured by chemical or physical methods. The only property by which such an active principle can be recognised and measured is its action on the living animal or surviving organ, which must somehow be made the basis of what is called a "biological standardisation" or "biological assay."

You will probably have observed that it is in relation to the more recently introduced types of remedial agents that such methods have found their chief application. Such newer remedies have this in common, that they aim at dealing with the causes of disease, by directly replacing defects, or directly reinforcing natural functions or defensive reactions, and not merely at alleviating or palliating symptoms, as do so many of the older medicines, as well as their modern, synthetic substitutes. The use of natural remedies dealing with causes—the antitoxins and immunological remedies, the hormones and the vitamins—is a relatively modern development. It began to become effective only a little before the opening of the present century, and has therefore a history of only some 40 or 50 years, in comparison with the age-long use of the unnatural medicines modifying symptoms, the origin of which goes back to the very beginnings of recorded history. Practically none of these natural remedies, when they first come under investigation and are first applied, can be assayed by methods of ordinary analysis. In one case or another, indeed, the progress of research, promoted by a common notation of biological activity, has succeeded in isolating the active hormone or vitamin, and has thereby enabled an adequate chemical method for its measurement to be devised, or has even led to the synthetic production of the pure principle, and the use of this in medicine, in place of a crude extract requiring standardisation. But though such chemical progress has been astonishingly rapid in recent years, even more rapid has been the emergence of newly discovered principles with great remedial potentialities, which, for the time at least, must have their activities measured by biological methods and recorded in a biological notation. For the present, then, and for some time to come, we shall have to regard methods of biological assay as necessary for a large, and probably a growing section of practical therapeutics, and for some of the most progressive departments of research in pathology, physiology and biochemistry.

DEVELOPMENT OF BIOLOGICAL ASSAY.—I propose briefly to review the history of the method, to glance at the nature and origin of some of the misunderstandings that have arisen with regard to it, and to trace the emergence of the principles which have enabled it to acquire a sounder scientific reputation, and to provide the basis for a world-wide uniformity of notation for a number of important remedies.

While, of course, some crude kind of measurement of the effect of drugs upon men and animals has existed since medicine began, and was given a greater precision when experimental pharmacology began to record the smallest doses of various drugs that would produce recognisable degrees of action, the earliest case known to me of the employment of an action on living animals as a basis for the indication of a dosage in units of activity, instead of in units of weight or measure, was that of the antitoxic serum obtained by immunising an animal, usually a horse, by injections of the diphtheria toxin. We know now that it differs from the normal serum in the proportion between the globulins and the albumins making up its proteins. For some years past it has been possible to detect the proportion of antitoxin which just neutralises a given toxin by observing the earliest appearance of an aggregation or precipitate in a series of such mixtures; and certain very recent developments have enabled the antitoxic moiety of the globulin to be split off by controlled and restricted enzymatic hydrolysis, and thus obtained in a more definite form. There are encouraging signs, therefore, that it may ultimately be possible to determine the specific activity of this and similar preparations by purely physical and chemical methods. At the time of its discovery, however, and for many years afterwards, there was no method known by which the presence of the antitoxin in a serum could even be detected, much less its quantity measured, except by testing its power of neutralising the action of the toxin on an animal sensitive to it. In France the attempt was made to do this by determining the dose needed to save an animal from an actual infection by diphtheria bacilli; in Germany they tried to do it by finding the dose of a serum which would neutralise a certain number of lethal doses—so-called—of a toxin. The results obtained on these lines were so confusing and misleading, that it required a research which is one of the classics of immunology, and, indeed, provided the basis for all true biological standardisation, to bring order out of the muddle. This was due to the genius of Paul Ehrlich, who, having thus put the assay of antitoxic sera on a sound basis, and opened new fields to exploration in the science of immunology, turned his attention to the systematic search for artificial synthetic remedies for infections, discovered salvarsan, and inaugurated the new science of specific chemotherapy, which, as yet, has only begun to show its great potentialities.

Ehrlich must have observed that the term "minimal lethal dose" of a toxin had in itself no precise meaning—a point to which we shall later return. The point, however, of special interest and importance was his discovery that two toxins of equal toxic potency, as nearly as this could be measured, might require widely different proportions of the same antitoxin to neutralise their toxic actions.

He found the explanation for this anomaly in the fact that every sample of toxin contained a variable proportion of material which had lost its toxic action, but retained its affinity for antitoxin. He saw, then, that the only way to order and safety, out of this confusion, lay in the establishment of a fixed, stable, standard sample of completely desiccated antitoxin, sealed up in dry vacuum, and kept in cold storage. The unit of antitoxin was defined, once for all, as the neutralising or binding-power of a given weight of this dried serum sample. The test dose of any toxin was the smallest amount which, when combined with this unit, would leave sufficient toxin free to kill a guinea-pig in a standard period of 4 days; and, when the test dose of a particular toxin had so been determined, the volume of any serum containing one unit could be ascertained by mixing a close series of dilutions, each with the test dose of toxin, and finding which mixture left just enough toxin free to kill a guinea-pig in the standard time.

There is one point about this and similar methods, in which the unit of a serum neutralises a large number of lethal doses of a toxin, which deserves special notice. Let us suppose that the number of binding doses of a particular toxin which the serum just neutralises is 1000. Then, theoretically, the test dose of the toxin contains 1000 binding doses + 1 lethal dose; but you will see that the accuracy of the determination would not be seriously affected if the dose actually determined left free 5 lethal doses instead of the theoretical single lethal dose, the difference of 4 lethal doses involving an error of only a very small percentage of the total number involved in the test. Under such conditions the variations in the sensitiveness of the different guinea-pigs in a test series, inevitable even when their ages, weights and all other conditions are kept constant, become practically of small account. The guinea-pigs are simply indicators in a titration, and the fact that their sensitiveness may vary over a certain range introduces an error not seriously greater than that caused in acidimetry by the addition of phenolphthalein, for example, in an amount not accurately measured. The point has real importance, because I strongly suspect that the accuracy obtainable in such an antitoxin titration, even with only one or two guinea-pigs on each mixture, led to the erroneous assumption, from false analogy, that the single lethal dose of an unmixed poison could be determined with comparable accuracy, with the use of one, or at most a few animals on each dose. It took, in fact, a good deal of work and advocacy at a later stage to eliminate this delusion, and to convince those concerned that the expression "lethal dose," or "minimal lethal dose," had no real meaning. The point, however, which I wish specially to emphasise, as established by Ehrlich's work on antitoxin standardisation, is that a biological assay or standardisation, like any other standardisation or measurement, must be comparative, and made in relation to a fixed and invariable standard of reference.

Ehrlich had unfortunately used the term "minimal lethal dose" in connection with his antitoxin standardisation, but had escaped the misleading assumption that the phrase implies, because, as I have suggested, he was determining only the end-point of a titration. This was not the case with the many attempts to measure the activity of toxic or physiologically active substances directly, in terms of a lethal effect, or other limiting animal reaction. The first instance of this kind was the attempt to standardise preparations of digitalis, by determining the dose required to stop a frog's heart in permanent contraction. One might suppose, from some of the writings on the subject, and the frequent reference to "frog units," that there was a sharp line, or at most a narrow margin, between the dose per gramme of body weight from which every frog would recover, and the dose per gramme that would kill every frog receiving it. Such an idea would, of course, be very far from the truth. I believe that Greenwood was the first to point out, in a study of figures obtained by Rowland for the lethal effect of different doses of a plague-bacillus toxin on rats, that there was a wide range of doses, within which the question whether a particular animal would die or survive was a matter not of certainty, but only of statistically calculable chance. A good many years later Trevan, in a very valuable and effective paper, clearly indicated that the term "minimal lethal dose," which had become so prevalent in biological literature, had no clear or proper meaning. It might mean, either the smallest dose capable of killing even one animal of a very large number receiving it, or the smallest dose which would not allow even one to survive. Though in certain rare cases these two values might be fairly close together, in most cases, and in all those for which a biological standardisation had been found necessary, there was a wide disparity, the certainly lethal dose being several times, and often many times, that which would still kill occasionally. These doses at the extremes of the whole lethal range, moreover, were not capable of exact determination, the curves relating dose to proportionate lethality being S-shaped, and becoming asymptotic to the abscissa at each end. The range in which the dose producing a certain effect can be measured with most precision is not at the ends of the curve, but at the middle point, where the dose kills about one-half of the animals injected. We ought, therefore, as Trevan suggests, to speak, not vaguely of a "minimal lethal dose," but of a dose lethal for a stated percentage of animals, choosing for assay purposes a dose falling on the steepest part of the graph relating mortality to dosage. Obviously, on a limited number of animals, even this dose cannot be determined exactly, but only within a certain range of probable error. We can experimentally determine the "standard deviation," and calculate the frequency with which the result will have a given degree of inaccuracy. We can thus make allowance for any desired approach to certainty, but no more. The cold blast of statistics has had a bracing effect, and has swept away a good deal of flimsy assumption with which the subject was cumbered. It is of curious interest to recall how the number 3 seemed, at one time, to have a mysterious attraction or significance for workers in this field. We were recommended, for example, to find the dose of a digitalis preparation which would kill 2 out of 3 frogs injected, and to regard this as the lethal dose; it seemed to give to some an added confidence, if such a result was stated as "a 66·6 *per cent. mortality*." Later, we were recommended to test a selected dose of an insulin preparation on rabbits until we found three consecutive rabbits giving the same fall of blood sugar, and then to accept this result as giving a true measure of the activity; a method, as I once remarked, for which the only recorded authority was the Bellman in *The Hunting of the Snark*, with his pronouncement that "What I tell you three times is true."

PRINCIPLES OF BIOLOGICAL STANDARDISATION.—Gradually, by the application of sound reasoning and statistical analysis, the subject has been lifted above such facile assumptions and credulous optimism, and we know much more clearly how the nearest approach to quantitative accuracy can be secured, and, in each particular case, how wide the limit of inevitable error remains. Some years ago I ventured to put forward certain general principles, to which any biological standardisation ought to conform. I would maintain them still, with modifications only of the details of their application in particular cases.

(1) Like any other standardisation or measurement, it is essentially comparative, and must be made in relation to a fixed, material standard. Apart from individual variations among a common stock of a species of animal, the sensitiveness of a whole stock may vary in unknown ways and to unknown degrees with season, temperature, diet or other unrecognised conditions. There can be no such thing as a frog, mouse, or rabbit unit; the animal can only serve as a reagent in a strictly comparative test.

(2) The standard chosen must owe the activity, which the test measures, to the active principle for which the preparation is to be assayed.

(3) Provided the biological reaction used in the test affords a means of measuring a known active principle with sufficient accuracy, it need have no relation to the therapeutic effect. It has often been suggested, quite absurdly, that the comparative assay of digitalis by use of the permanent stoppage of a frog's heart as an end-point reaction must give results having no relation to its therapeutic value, because digitalis is used in medicine to strengthen the hearts of men and not to stop those of frogs. It would be as rational to argue that a colorimetric assay, which also depends, in the reading, on a biological reaction, can have no value, because the drug assayed is not used in medicine to produce a colour.

(4) The best type of test, when it is available, is one in which the standard and the preparation under test are compared in succession on the *same* animal or preparation. Individual variation is thus completely eliminated, and we have only to allow for a change of sensitiveness with the progress of the experiment, which can be discounted by alternation of dosage.

(5) Usually, however, no such method can be used. We often have to depend on the observation of what my friend Prof. Gaddum has termed a "quantal" response—the presence or absence of some recognisable, limiting response in each of a series of animals. It is then that we have to introduce statistical considerations, and to calculate, in each case, the number of animals on a dose which will suffice to enable us to determine the strength, with sufficient accuracy for practical purposes, by observation of the proportion showing the "quantal" response. In other instances, we observe the degree of a measurable effect—such as a gain in weight on a vitamin dosage, or a fall in blood sugar produced by insulin. In such cases also we must use sufficient numbers to reduce the error due to individual variations, and we must, as always, give the test a comparative basis by simultaneous measurement of the effect of a known number of units of the standard preparation, upon a strictly comparable group of animals from the same stock, and subject to identical conditions. When the effect is evanescent, as that of the fall of blood sugar produced by insulin, we can

eliminate individual idiosyncrasy, though not the day-to-day variation shown by a single individual. This is effected by using the same two groups of animals on two occasions, at a suitable interval, giving group A the standard and group B the sample under test on the first occasion, and reversing the order on the second; so that the response of every animal in both groups, to both standard and sample, can be used in comparative calculation of the strength of the sample.

The most fundamental of these principles, applying to every case, is that the standardisation is made by a comparative test, in relation to a fixed standard, in terms of which the unit of activity is once for all defined. The unit is the fixed value, which must remain unchanged even when a new standard has to be made for replacement, or because a better material for it becomes available. Such a system keeps the unit fixed, and provides, in the material standard, a currency for its transmission all over the world. Under these conditions, as the unit becomes generally adopted, the results of scientific work in all countries become comparable by the use of a common quantitative notation, and the greatest freedom can be allowed in experiment directed to the improvement of existing methods, and the discovery of better ones, for applying the common standard in comparative measurements.

INTERNATIONAL STANDARDS.—These principles have provided the basis of action in the creation, since 1921, of a large series of International Standards for therapeutic agents, the activity of which can only be determined by comparative biological tests. At various stages, and in relation to successive substances of this kind, it has been necessary to stand firmly for the principle of fixed material standards, and units defined in terms of them, and to resist the common tendency of investigators to invent and promulgate units of their own, defined in terms of some animal reaction which they have found it convenient to observe. Time and again, when the question of international action for the standardisation of some substance has arisen, it has been found that the subject is already encumbered and common action compromised by the existence, for the one substance, of a whole series of different and incommunicable units, promulgated by different investigators, each basing his definition on some animal reaction which he has found convenient, and which, with a constancy of conditions unattainable outside his own laboratory and his own stock of animals, he believes that he can measure with a sufficient uniformity. In repeated instances it has become obvious that, even with animals of the same stock, but kept in different laboratories, small variations in age, diet, prevalent temperature and other conditions may lead to widely different values for a unit, if it is thus defined in terms of an animal reaction. And in every case the only way to uniformity has been found in the creation of a common material standard, and the definition in terms of it of a common unit, independent of the nature of the test chosen for its comparative measurement.

The international work began in 1921 in connection with the Health Organisation of the League of Nations, on the initiative of Dr. Thorwald Madsen, Director of the State Serum Institute, Copenhagen. Before the war the whole world had depended for samples of the standard for diphtheria antitoxin on the goodwill of Ehrlich's own Institute in Frankfurt, where the original standard of dried serum had been adopted and was preserved. Subsidiary standards, with unit values determined by exact comparison with Ehrlich's, had fortunately been set up in a number of other countries, and particularly, on a national basis, in the Public Health Department at Washington. Otherwise the outbreak of war, shutting off most of the world from access to the original, basic standard kept in Frankfurt, might have led to confusion and discrepancy between the units used in different countries for measuring and indicating the activity of this important remedy. With the object of discovering the extent to which such discrepancies had, in fact, arisen, and of providing against the recurrence of such uncertainties, the first International Conference dealing with such matters met in London in 1921, on the initiative of the Health Organisation of the League of Nations, and with Dr. Madsen as President. It is worthy of notice, I think, that this Conference had interest and value apart from its result in recorded and effective agreement. It provided, I believe, the first occasion for the meeting, in friendly discussion, with the express object of practical agreement on a scientific matter, of experts from the different countries so recently at war; for, like all the subsequent Conferences having a similar purpose, the experts invited to attend it were chosen on a scientific and not on a political basis, and without any reference to membership of the League. It is much to be regretted that in recent years a new, political attitude has intruded, through the refusal of countries which have withdrawn from the League to allow their experts to continue to participate in such scientific activities for the common good.

The first Conference, in 1921, accepted Ehrlich's unit for dipheria antitoxin, and arranged for the production of a new, international standard preparation, in terms of which that unit could be re-defined. This is now deposited, for custody and distribution, in Dr. Madsen's Institute, the State Serum Institute, Copenhagen. The second International Conference, under the same auspices, met in Paris in 1922, to deal similarly with tetanus antitoxin. They adopted as a basis the American Standard, but, unfortunately, not without a gratuitous change from the American value in defining a unit for international use. This was a rare example of the intrusion of other than strictly scientific considerations into this international activity; and it has contributed to the difficulties which have left the basis of the standardisation of this important serum still, at the present moment, short of a final, international agreement.

A little later Dr. Madsen, whose own special field is immunology, approached me concerning the possibility of doing something towards international uniformity in the standardisation of remedies of other kinds—drugs, hormones and others—for which biological methods were required and had been applied. It seemed possible that we might do something about digitalis and its allies, and about hormone preparations, such as those of the pituitary posterior lobe and the then newly-discovered insulin. It was obvious that something ought to be done, if possible, for the position was no better than chaotic. My then colleague, Dr. Burn, now Professor of Pharmacology at Oxford, had been conducting with me a survey of the activities of the different preparations of the posterior-pituitary extract obtainable in this country; we had found that, in respect of the activity as a stimulant of the uterus to contraction, for which the extract was widely applied in obstetrics, the different preparations varied over such a range that the strongest had 80 times the activity of the weakest. Even in one country, then, preparations all labelled "physiologically standardised," and offered for use, mostly in emergency, with the same dosage, could be completely ineffective at one end of the scale, and strong enough to threaten rupture of the labouring uterus at the other. As for insulin, with its peculiar need for accurate adjustment of dose, in that a relatively small excess might produce a dangerous condition while a small under-dosage would cause relapse, already some three different rabbit units and a mouse unit had been proposed, and nobody knew clearly their relation to one another, even if any of them had been accurately and consistently measurable in different laboratories. The travelling victim of diabetes had a poor prospect, indeed, of obtaining the immense benefits of this new treatment with safety and regularity, as he wandered from one country to another. There was clearly an urgent call for prompt international action in these cases, and an international Conference of experts met in Edinburgh in 1923, and took the first steps towards it. Digitalis and its allies, pituitary posterior lobe extract and insulin were the chief subjects of discussion, with side-glances at the possibility of action in other directions. After some three days of discussion, most vigorous and obstinate in the case of insulin, the Conference unanimously agreed to organise and carry out co-operative tests of the suitability of dry, stabilised standards for these three main items of our discussion. The late Prof. Magnus of Utrecht undertook to prepare such a standard for digitalis, and Prof. Voegtlin of Washington accepted the responsibility for the pituitary standard. When the advocacy of rival animal units for insulin had reduced their activities to exhaustion and deadlock, the members of the Conference also agreed to consider the definition of a common unit, independent of methods, in terms of a dry, stable standard preparation of insulin, though they were sceptical as to the possibility of making one. I was in the fortunate position of being able to state with confidence that, if we were given the supplies of insulin, my late colleague, Dr. H. W. Dudley, had a method ready for making the stable standard. When the same group of experts, with others added to their number, met again for a fuller discussion at Geneva, in 1925, the data for agreement were all to hand, as the result of really international, co-operative trials in the intervening years.

Insulin Standard.—Everybody concerned was ready to ignore fractional discrepancies, and to agree forthwith that the new standard for insulin should be regarded as having 8 *units of activity in* 1 *milligramme*. Thereafter it did not take long to secure the adoption, throughout the world, of one common unit of insulin, as thus defined. Dudley's standard preparation, then adopted, remained current and authoritative till 1935. By that time the late J. J. Abel's success in obtaining insulin in the form of crystals, and the later discovery by Scott, of Toronto, that the crystals were a zinc salt of insulin, had made it possible to obtain crystalline insulin, as a pure and regularly reproducible product, in any amount required. The original, impure standard being then within measurable distance of exhaustion, the opportunity was taken to make a new standard of the crystalline substance, in sufficient quantity to last for very many years; and the unit value of this was again determined in a number of institutions in several countries, by elaborate, comparative assay, in terms of the original standard of 1925. There followed a good deal of discussion as to the precise unit value to be assigned to the new standard, ending in agreement to regard it as containing 22 *units per milligramme*; and on that basis the unit of insulin ought now to be fixed for all time, or for so long as insulin preparations still need to be assayed by biological methods.

Pituitary Posterior Lobe Extract Standard.—For this extract the Conference of 1925 readily accepted the dry standard, but spent much time, unwisely as it seemed to me, in trying to find an agreed strength, in terms of that standard, for a watery extract to be used in all countries and for all purposes. Immediately we came up against the differences of practice and experience in different countries. It appeared that the surgeons and obstetricians of one country would use with cheerful confidence doses which those of other countries regarded as desperately dangerous. Here again, we found a way out, and a basis for ready agreement, in the definition of a unit in terms of the new standard, leaving it a matter of choice, in different countries, to inject ten or two of such units for the same purpose, in accordance with the varying standards of caution and courage in the practitioners, and of sensitiveness or toughness in the patients. Again, therefore, the notation, though not the practice, of the whole world was unified. The original definition of this unit had reference particularly to the activity of the pituitary extract forming the basis of its chief use, in obstetrics. It remained only for later conferences to define similar units, in terms of the same standard, for the other principles contained in this extract, acting on the circulation and on the excretory function of the kidney. These units, I hope, will now stand so long as these pituitary principles require biological assay. Arrangements are now in prospect for replacing the standard, of which a large part has been used, by a new one, in terms of which these units will have to be separately re-defined, without any change in the value of any, so far as careful comparison by a number of experts can avoid it.

Digitalis Standard.—Although the standard sample of digitalis was readily accepted, the conservative attitude of the pharmacologists from most countries did not, at the 1925 Conference, allow them to accept immediately the idea of a unit of activity for so old-fashioned a remedy. They preferred to aim at enforcing a conformity, in the activity of all digitalis used in medicine, to the strength of the accepted standard, by judicious blending of strong and weak samples. To me this procedure always seemed more suitable to the grocery or the spirit trade than to scientific medicine, and a later Conference was persuaded to define a unit of activity for digitalis also. The advantage of this was manifest in 1935, when it became necessary, in due course, to introduce a new and more carefully prepared standard to replace the original one, which had been rather rapidly exhausted by the demand. It was much easier and better to decide, on the basis of co-operative, international comparisons, *that the unit, defined as the activity of* 100 *milligrammes of the old standard, was represented by* 80 *milligrammes of the new one*, than it would have been to hunt for inactive or spoiled samples of the drug, in the hope that these, by suitable blending, would reduce the activity of the new and more perfect material to that of the original standard. The British Pharmacopoeia, which had led the way by adopting the unit basis for digitalis in its 1932 issue, was able to adjust its indications to the new standard by a simple numerical change, made in the corrective Addendum issued in 1936.

Standards for Synthetic Organic Compounds.—The Conference of 1925 had under consideration a group of remedies of a different kind, with regard to which it had been feared that any effort to create international standards would encounter unusual difficulties of national prestige and commercial jealousy. This was a group of synthetic organic compounds containing arsenic, including Ehrlich's salvarsan, with neosalvarsan and certain other derivatives. These were, in theory, known chemical substances, and there could be no question of standardising them in biological units. Their physical properties, however, made it impossible to prepare them pure, and small variations in process had been found to make them, on the one hand, dangerously toxic, or, on the other hand, weak in therapeutic action. It was necessary to provide standard samples, by comparison with which agreed maxima of toxicity and minima of potency could be determined; and when it came to the point, the fears of international acrimony proved to be ill-founded, and standards were readily adopted, which, in spite of the new political difficulties of recent years, are still maintained with the co-operation of the laboratory from which these substances originated.

Extensions of the System of International Standards.—I have spoken in some detail of these early activities in the creation of international standards, not because their direct results were more important than many others that have followed, but because they were effective in establishing traditions and principles on which subsequent action has been based. I must be content with a more rapid review of these later extensions of the system of international standards, to other members of those groups of remedies with which a beginning was made in these earlier years, and to other groups which only later came under effective consideration. Standards for a number of antitoxic and other curative sera have, at several stages, been added to the list, and, by reference to the units based on these, it has been possible secondarily to standardise certain antigens used for the production of an active immunity. The desirability of unification, by international agreement, of the units used in measuring different types of *vitamin activity* was already under discussion at the Geneva Conference in 1925, but only in the sense of an attempt, fortunately abortive, to obtain international recognition for certain detailed methods of testing. The time was not ripe for effective action concerning these important, protective constituents of natural foods, till 1931, when a first International Vitamin Conference, under the auspices of the Health Section of the League of Nations, met in London under the chairmanship of Sir Edward Mellanby. They had to deal with a position largely analogous to that which had earlier been encountered with regard to other classes of remedies—a multiplicity of rat, pigeon or guinea-pig units, each claiming a special convenience, or special accuracy for a particular criterion or end-point, but all subject to the widest variations with small changes of conditions, and none affording any basis of comparison between the values obtained for the same vitamin by the different methods. And here, again, the only basis for agreement and unification was found in the acceptance of stable standards, in terms of which it was easy to define units, which would remain valid and unvaried whatever the tests used for their comparative estimation in relation to the standards. In several instances later Conferences, or agreements by correspondence among members of earlier ones, have been able to substitute better vitamin standards, consisting of pure, synthetic substances, for the original standards made of the crude materials available at the time of their adoption; but all these new standards have been very carefully evaluated in terms of the old, and the units re-defined so as to involve the smallest unavoidable change of value with change of standard. As an example of the scale of accuracy attainable in such work, I might mention the recent adoption of pure, synthetic *Aneurin* as the international standard for vitamin B_1, in place of the crude adsorption product which formed the original standard. The international comparisons of these old and new standards were made by a whole range of different methods, both prophylactic and curative, on rats and pigeons. Under such a wide variety of conditions, it seemed certain that the comparisons would be affected, in widely different degrees, by differences in the rates of absorption of the vitamin, when given, respectively, as a pure substance and as a crude extract adsorbed on clay. Nevertheless, in the results from all sources and by all methods, the extreme values assigned to the unit were 2γ *and* $3{\cdot}5\gamma$ *of the new, pure standard,* and the large majority were round about 3γ, which was also the precise average of the whole series. There was no difficulty in adopting 3γ, by unanimous agreement, *as the quantity of the new standard containing the unit.* And this new definition, being in terms of a chemically pure substance, should now stand for all time, or for as long as this vitamin continues to be measured in units of activity.

Standardisation of Sex Hormones.—Precisely the same principles have been followed, I am bound to say with less practical and lasting success, in adopting standards and defining units for the sex hormones. We adopted a standard of pure oestrone for oestrogenic action, and defined a unit in terms of it, in the hope of saying good-bye to mouse-units and rat-units. Then came *oestradiol,* and the discovery that attempts to assay it in terms of oestrone units gave widely different results on different species, and with different methods of administration. The ideal of a single standard and unit, independent of method, would not hold as between these different forms of the hormone. It would have been easy to conclude that we must have a different standard for each form; but, on the one hand, it was never possible to know in what relative proportions they would be present in a crude extract, and, on the other hand, manufacturers, with a perverse enterprise and ingenuity, were soon busy with the production of artificial esters, with which the variations of unitage in terms of the original hormone, produced by different methods of administration to different kinds of animal, became even more fantastic; we certainly could not produce a new international standard for every new proprietary ester. Much the same is happening in connection with the male hormones, *androsterone* and *testosterone,* and their artificial esters. When we take note, in addition, of the recent appearance of relatively simple and easily made synthetic substances, like the so-called *stilboestrol,* closely similar in their action to the natural hormones, but stronger, I think we may reasonably forecast a fairly early disappearance of biological standards and units from this particular field, and its replacement by an ordinary dosage in terms of exact weights of pure substances. And I think that all the signs point to a similar change in the field of the vitamins, where identification as pure substances, and the production of these by artificial synthesis, are now proceeding so rapidly as to overtake and outpace the description of new vitamins. The death-rate, so to speak, of vitamins identifiable only by letters of an alphabet threatened with exhaustion, is at last happily in excess of the birth-rate.

In both these fields, then, we may be able to foresee the end of biological standardisation—a consummation, I venture to say, devoutly to be wished. Meanwhile, however, I would also venture to claim that, even in these fields, the precision given to biological measurement and the comparability of the results from different laboratories, obtained by the establishment of fixed international standards and units, has been a powerful factor in the rapid advance of true chemistry in these fields, and thus in the accelerated progress here of biological standardisation towards its proper goal of self-extinction. The international units will further have provided, at least, a bridge by which the mind of the practical physician, never eager to jump a step in calculation, may be able to pass over the gap between dosage of crude extracts in units and dosage of pure substances in milligrammes. Meanwhile the work of unification is advancing into other fields, and only last summer a Conference at Geneva adopted and defined four new standards, and units in terms of them, for two complex, and, hitherto, chemically intangible hormones of the anterior pituitary lobe, and two analogous principles formed, during pregnancy, in the blood serum and the urine of certain animal species. These are now in course of preparation, and will, in due course, be ready for addition to the already quite imposing series of standards, with corresponding units, which international action has produced.

The following table includes a complete list of the International Standards hitherto adopted and gives an indication of the weight of each representing one unit, and of their distribution, for custody and administration, between the Copenhagen and Hampstead Institutes.

ORGANISATION OF STANDARDISATION.—From the first the International Standards for antitoxic and other sera and immunological remedies have been committed to the care of the State Serum Institute at Copenhagen. My own early association with the international work on the standards for drugs and hormones led to the custody of these being entrusted to the National Institute at Hampstead. In due course the Institute came to be regarded as a kind of international "Pooh-Bah" in these matters, with a responsibility for "everything else" in the way of standards, other than the serum standards. The Therapeutic Substances Act of 1925 brought under State control in this country, for the first time, the production and standardisation of all the sera, salvarsan (arsphenamine) and its derivatives, insulin and post-pituitary extract, and laid on the National Institute the responsibility for preparing and providing national standards, based in all cases on those which had been internationally adopted. We were ready to fulfil this obligation before the Act became effective in 1927. For some of the sera subsidiary standards had to be prepared, and the units defined in relation to them, by exact comparison with the International Standards. For others we ourselves prepared the first standards, of which portions were internationally accepted, and transferred to Copenhagen for international use. In the preparation of the salvarsan standards we had co-operated with Ehrlich's Institute, the Georg Speyer

Haus at Frankfurt, and the preparation of the insulin and pituitary standards had been in our hands from the first. When a second standard for insulin was required, consisting of the pure, crystalline hormone, this was prepared in the home of insulin, Toronto, and a suitable portion was allotted for distribution in the Old World, the American continents drawing their supplies from Toronto. When further national standards were required by the British Pharmacopoeia of 1932, we had those for digitalis and strophanthus ready, as well as those for the vitamins,

INTERNATIONAL BIOLOGICAL STANDARDS

No.	Standard preparation	Adopted in	International unit milligrams	International distributing centre
1	Diphtheria Antitoxin	1922	0·0628	State Serum Institute, Copenhagen.
2	Tetanus Antitoxin	1928	0·1547	
3	Antidysentery Serum (Shiga)	1928	0·0500	
4	Antipneumococcus Serum (Type I)	1934	0·0886	
5	,, ,, (Type II)	1934	0·0894	
6	Staphylococcus α-Antitoxin	1934	0·500	
7	Gas Gangrene Antitoxin (perfringens)	1931	0·2660	
8	,, ,, ,, (Vibrion Septique)	1934	0·2377	
9	,, ,, ,, (oedematiens)	1934	0·2681	
10	,, ,, ,, (histolyticus)	1935	0·3575	
11	Old Tuberculin	1931	—	
12	Diphtheria Antitoxin for Flocculation Test	1935	—	
13	Vitamin A (mixed carotenes)	1931	0·001	
	(pure β-carotene)	1934	0·0006	
14	,, B_1 (adsorption product of vitamin B_1)	1931	10·0	
	(pure synthetic vitamin B_1)	1938	0·003	
15	,, C (*l*-ascorbic acid)	1934	0·05	
16	,, D (irradiated ergosterol solution)	1931	1·0	
	(calciferol)	1934	0·000025	
17	Arsphenamine	1925	—	National Institute for Medical Research, Hampstead, London.
18	Neoarsphenamine	1925	—	
19	Sulpharsphenamine	1925	—	
20	Insulin (dry insulin hydrochloride)	1925	0·125	
	(pure crystalline insulin)	1935	0·0455	
21	Pituitary (posterior lobe) powder	1925	0·5	
22	Digitalis	1925	80·0	
23	Ouabain	1928	—	
	Oestrus-producing hormones:			
24	(i) -oestrone	1932	0·0001	
25	(ii) -oestradiol monobenzoate	1935	0·0001	
26	Androsterone (for male hormone)	1935	0·1	
27	Corpus Luteum Hormone (progesterone)	1935	1·0	
28	Chorionic Gonadotrophin	1938	0·1	
29	Serum Gonadotrophin	1938	—	
30	Thyrotrophin	1938	—	
31	Prolactin, Galactin or Mammotrophin	1938	—	

which we had prepared and were holding also on the international account. The position will be the same when standards for the sex hormones and the anterior pituitary principles become official in this country; for in all these instances the standards have been prepared by us on behalf of the International Organisation, and portions set aside to constitute the official standards for this country. The National Institute, accordingly, has accepted, and is discharging, a triple obligation in relation to these standards—on behalf of the International Health Organisation under the League of Nations, of the Administration of the Therapeutic Substances Act and of the British Pharmacopoeia; although we arrange for these functions to overlap so far as is proper and convenient, they are not coterminous. The International Standards are distributed all over the world, in some instances to as many as 33 countries. Wherever possible we send them to National Control Centres, charged like our own with the duty of making equivalent national standards, or, for some standards, with the further distribution, in their respective countries, of supplies of the international standard material furnished for the purpose.

You might suppose that this work would involve a large department, with a numerous staff giving whole time to the work. It has not done so. My colleague, Dr. Hartley, who acts as Director of all our Standards work, has indeed given a large part of his time to it over the past 17 years, devising the methods by which the standard preparations are prepared and stabilised in our own and many other laboratories, and making himself responsible with the administrative staff of the Institute, in particular with Dr. Chalmers, now our Medical Administrative Officer, for the complex organisation which the growth of the work has entailed. Much of the investigatory work has been undertaken by our colleagues on the regular Research Staff of the Institute, in our sections of Bacteriology, Pharmacology and Endocrinology, who have accepted various items, as they have arisen, as parts of their research programmes. A theoretical case could, I think, have been made for a separate department charged with these important duties, and separately financed, instead of distributing the work through the Institute, supported from the general research funds of the Medical Research Council, apart from a small annual contribution from the League of Nations. In practice, however, I am inclined to think that we adopted the better plan; for I believe that, if work of this kind is to be done with the right spirit of enterprise and initiative, it is often done best by those engaged also in wider fields of research; and I believe, also, that many men engaged in more fundamental researches into the unknown can strengthen their equipment, by some degree of contact with work directed to providing the means of quantitative precision, consistency and uniformity, in the practical application of what is known already.

NATIONAL INSTITUTE FOR MEDICAL RESEARCH
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The Ultra-Violet Absorption of Calciferol

By S. K. CREWS, Ph.C., A.I.C., and E. LESTER SMITH, D.Sc., F.I.C.

PUBLISHED figures for the ultra-violet absorption ($E^{1\%}_{1\,cm.}$ 265*mμ*) of calciferol (vitamin D_2) vary from 495 to 460.[1,2] Suggested standards have been put forward[3,4] including those of the Monograph in the 1936 Addendum to the B.P. 1932.

It was found that the spectrophotometric determinations of calciferol carried out in the analytical departments of The British Drug Houses, Ltd., and Glaxo Laboratories, Ltd., were not in agreement, although determinations made on solutions of potassium nitrate and potassium chromate did agree; a collaborative investigation of these discrepancies was therefore undertaken by members of the scientific staffs. For this purpose operators exchanged plates and samples and visited each others laboratories to compare techniques.

PHOTOMETERS.—Of the three instruments used in this investigation, two were fitted with Spekker photometers and the third with a modern short-focus rotating sector photometer. In all the experiments the light source used was a condensed spark between tungsten steel electrodes.

TABLE I

Instrument		Calciferol "A" $E^{1\%}_{1\,cm.}$ 265*mμ*	Calciferol "B" $E^{1\%}_{1\,cm.}$ 265*mμ*
Sector photometer	..	412·5	421
Spekker photometer	..	430*	475

* 0·0416 per cent. solution in 1-mm. cell. Same solution diluted 1 : 20 in 1-cm. cell gave a value of 445. Total times of exposure 43 seconds and 5 seconds, respectively.

It was shown that the "spotting" in the two laboratories of the same spectra on the plates led to no significant differences in the values deduced therefrom. Different samples of calciferol all gave appreciably lower values for $E^{1\%}_{1\,m.}$ 265*mμ* when examined with the rotating sector instrument than with the others (see Table I). The time of exposure of the calciferol to radiation was very much longer in this instrument than in those equipped with Spekker photometers, and it soon became apparent that shorter exposures led to higher values. If the same calciferol solution was used for successive determinations and was thus subjected to increasingly prolonged irradiation, decreasing values were obtained; this result was obtained in both laboratories. (See Tables II and III.) It was also established that the rate of photo-chemical change was about the same in isopropyl alcohol as in cyclohexane solution (see Table IV).

TABLE II

Instrument	Total time of exposure Seconds	Calciferol "A" 0·0022 per cent. in isopropyl alcohol in 1-cm. cell		Calciferol "B" 0·002 per cent. in isopropyl alcohol in 1-cm. cell	
		$E^{1\%}_{1\,cm.}$ 265*mμ*	Per cent. of initial E	$E^{1\%}_{1\,cm.}$ 265*mμ*	Per cent. of initial E
Sector photometer	34	469	100	483	100
	79	404	86	446	92
	106	375	80	411	85
	129	346	74	371	77

TABLE III

Instrument	Total time of exposure Seconds	Calciferol "C" 0·0406 per cent. in ethyl alcohol in 1-mm. cell		Total time of exposure Seconds	Calciferol "B" 0·0409 per cent. in ethyl alcohol in 1-mm. cell	
		$E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	Per cent. of initial E		$E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	Per cent. of initial E
Spekker photometer (1)	32	470	100	18	465	100
	101	425	90	85	440	95
	133	410	87	164	405	87
	182	395	84	225	380	82
	230	370	79	286	370	80
	281	345	73	—	—	—
Spekker photometer (2)	3	503	100	—	—	—
	33	487	96·8	—	—	—
	108	437	86·9	—	—	—
	210	412	81·9	—	—	—

TABLE IV

Instrument	Total time of exposure Seconds	Calciferol "D" 0·002 per cent. in iso-propyl alcohol in 1-cm. cell		Calciferol "D" 0·002 per cent. in cyclo-hexane in 1-cm. cell	
		$E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	Per cent. of initial E	$E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	Per cent. of initial E
Sector photometer	38	491	100	507	100
	69	447	91	458	90·3
	98	421	85·7	435	85·8
	125	397	80·8	410	80·8
	157	361	73·5	373	73·5

TABLE V

Instrument	Batch No.	Normal technique $E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	Continuous flow method $E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$
Spekker photometer (1)	"E"	460	485
	"F"	475	485
	"G"	475	490
	"H"	480	490
	"I"	475	490
	"J"	480	490
	"K"	480	500
Spekker photometer (2)	"L"	476 (2 secs.)	—
	"M"	495 (3 ,,)	—
	"N"	503 (3 ,,)	—
	"O"	495 (2 ,,)	495 (2 secs.) 12 ml. per min.
		446 (102 ,,)	495 (2 ,,) 104 ,, ,, ,,
	"P"	480 (2 ,,)	—
	"Q"	478 (2 ,,)	—
	"R"	488 (2 ,,)	—

Determinations were also made in a special cell, arranged so that the solution flowed through the cell during the spectrophotometric determination. In this way slightly higher values were obtained than by the normal technique with the shortest possible exposures and the smallest number of exposures necessary to determine the absorption at the maximum of the curve (see Table V).

It seems that the extreme photo-lability of calciferol necessitates special precautions for the accurate determination of its absorption spectrum, even when the most suitable instrument is used for the purpose. It should, moreover, be realised that the risk of error from this source is frequently present in determinations of absorption spectra in the visible region of the spectrum (including visual colorimetry) as well as in the ultra-violet.

In our opinion the continuous-flow method offers the most accurate means of determining the extinction coefficient of calciferol and other similar substances whose absorption spectrum is affected by exposure to ultra-violet radiation.

Our thanks are due to Mr. J. H. Singer and Miss B. E. Stern for assistance with the spectrophotometric determinations, and to the Directors of Glaxo Laboratories, Ltd., and The British Drug Houses, Ltd., in whose laboratories this work was carried out, for permission to publish these results.

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GREENFORD, MIDDLESEX
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Notes on the Examination of Textiles in Cases of Suspected Dermatitis

BY H. E. COX, D.Sc., Ph.D., F.I.C.

(*Read at the Meeting, May* 5, 1939)

ALL those who have had experience of cases of dermatitis alleged to arise from contact with articles of clothing or materials which are worn next to the skin, will agree that they often present much difficulty. It is now fairly well established that certain chemicals are irritant and when these are present the chemist feels himself on sure ground with regard to his part in the matter. But it happens in a great number of cases that no substance that could ordinarily be regarded as irritant is present or that substances which are present are only in such quantity as is normal to the particular garment. So the analyst may have not only to determine what is present, if anything, but he must be able to give some indication as to the importance or quantitative significance of what he finds. Both these problems are often really difficult.

The legal aspects of claims have been somewhat clarified by certain recent judgments of the courts. These have set out more distinctly the relations between buyer and seller or manufacturer; but they have also, in my opinion, brought more clearly into relief the scientific difficulties—both medical and chemical—and they throw on the experts the onus of proving or disproving certain things which formerly did not appear to arise.

I will refer briefly to two or three cases of fundamental importance. The principles that these cases establish are fairly obvious once they are set out in the clear terms which our judges usually employ. In *Grant* v. *The Australian Knitting Mills*, the underpants complained of contained about 1500 p.p.m. of sulphur dioxide, and the Privy Council upheld the view that the disease contracted and damage suffered were caused by this sulphur dioxide, which connoted a defective condition of the garment. The plaintiff's skin was held to be normal. It is now well known, as shown by Trotman and Bramley[1] that stored wool may often contain up to 0·25 per cent. or more of sulphur dioxide, and there is no doubt that millions of garments are worn daily which contain such quantities of sulphite. So if the plaintiff's skin was normal might it not equally have been urged that so were the pants! In *Griffiths* v. *Peter Conway*[2] the result was otherwise; the garment was normal, but the plaintiff was not, and the Court of Appeal emphasised the point that the essential matter for the seller to know in such cases with regard to the purposes for which the article is required consists in the particular abnormality or idiosyncrasy from which the buyer suffers. The fact that these essential characteristics are not known by the buyer is immaterial. So it is apparent that when dermatitis follows the wearing of a garment and there is no clear cause for it, the question whether the sufferer is abnormal or the garment abnormal becomes paramount. The chemist can only deal with the garment, and even when dealing with this encounters great difficulties. Moreover, in cases of doubt the court will often have regard to the fact that the plaintiff's state was induced by something. Thus, in a recent case in which a very unlikely substance was suggested but strongly denied by the defence, the learned Judge said: "Unless I can find in the case some plain evidence which satisfies me that there is some cause of the state of the plaintiff other than some irritant substance in the suit of clothes . . . I am driven to the conclusion that *something* of that sort must have been there." It cannot be easy to determine whether or not an individual is normal towards a number of chemical substances or natural products; but it ought to be within the competence of the chemist to determine whether a garment is normal or not, and it is to this aspect that I wish to draw attention. What substances should be expected in various garments and what quantities of substances which are common in them? Further, what impurities or possibly nocuous compounds may be anticipated as being possible. The latter might seem to be superfluous, but in my experience it is not so, for one finds at times allegations of the presence of compounds which have not been used at all in the materials concerned, and could not ordinarily arise. Hence it may be useful to record a few points gathered from a rather extensive experience.

ACIDITY.—It is often alleged that the suspect garment was acid. Garments usually are; but how much and what acid is present, and is it excessive? Cotton fabrics, in my observation, usually show a faintly acid reaction ($p\mathrm{H} < 6{\cdot}0$) to litmus or lacmoid but not to methyl red; titration of the acid shows about 0·1 per cent. reckoned as sulphuric acid. Wool presents some difficulty. Undyed bleached wool is always acid to a relatively high degree, an apparent acidity of 2 or even 2·5 per cent. being common; dyed woollen cloth is generally less acid, and in my observation seldom contains more than 1·5 per cent., reckoned as sulphuric acid, and about 0·7 or 0·8 per cent. is usual. Methods for the determination of acids in wool have been critically examined by Barritt *et al.*,[3] and study of their paper shows the difficulties of the subject. In my view the distillation method is most convenient. It is important, too, to determine whether acetic or formic acid is present; this also may be done by distillation. A further point to be borne in mind is that the acidity of woollens commonly increases with age and exposure, and is influenced by the dyestuffs present. There is evidence (*cf.* P. R. McMahon and J. B. Speakman[4]) that the disulphide linkages are hydrolysed in light to sulphide and this may be oxidised to sulphite and sulphate. Again, with acid dyestuffs the colour is usually more fast to water when the *p*H is low; if the wool has been dyed from an acid bath a greater amount of the dye actually enters into combination with the fibres and less base is available to mineral acid.

Most rayons and union fabrics are slightly acid, but the acidity, on distillation from these materials, is usually less than 1 per cent.

In hat leathers acidity may be of much importance; it should be determined by the standard Proctor–Searle method, and when so determined should not exceed about 0·5 per cent. Direct titration methods give quite misleading results, and the Proctor–Searle method is not applicable to chrome or semi-chrome tanned leather; for these, Innes's procedure is available. Some idea of the nature of the acid may be gained by the Innes method,[5] which consists in observing the *p*H value of a 2 per cent. aqueous extract before and after dilution with 10 volumes of distilled water. If a mineral or strong acid is present the difference figure on dilution will be greater than 0·7. The presence of chromic acid or formic acid should also be investigated.

SULPHITE.—In view of the Australian Knitting Mills case, to which I have referred, sulphur dioxide is important. It is not usually present in cotton or rayon fabrics, but is common in wool—so much so that one may be permitted to doubt whether it can truly be regarded as an irritant to normal persons. The sulphite in woollen clothing is not all removed by washing or extraction with hot water. Quite a considerable quantity will survive two or more launderings. As complex sulphides and some hydrogen sulphide may be formed in wool by the action of light, it is essential to accuracy to use hydrogen peroxide (not iodine or bromine) for the oxidation when determining the sulphite by steam-distillation after acidifying with a few drops of phosphoric acid. If no phosphoric acid is added the natural acidity of the wool does not suffice to liberate all the sulphite; evidence can be adduced to show that the sulphite is in part combined with the wool. Trotman reports 0·25 per cent. as fairly common and 0·5 per cent. as occasional; in my experience 0·15 to 0·2 per cent. is more usual in bleached garments and in dyed woollens one usually finds none, or only an insignificant trace.

CHROMIUM.—On account of the well-known lesions produced in chrome workers the presence and significance of chromium in a case of alleged dermatitis requires careful consideration. Here, again, we are considering an element which is very widely used and is to be found in millions of garments. It arises in three principal ways: chrome tanning in leather such as shoes, gloves or jackets; as an after-chroming process in fixing or brightening the colours in hat leathers for example; as a mordant in the application of vat and other dyes to textiles. Whether any chromium is present at all is easily determinable; if it is present it becomes important to know (*a*) its state, anionic or cationic, and (*b*) how much, if any, is soluble; also what solvent should be used and at what temperature.

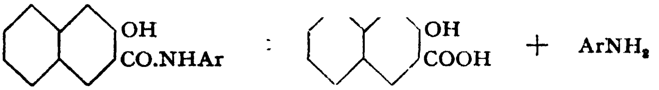
Chromates are undoubtedly more likely to be irritant than cationic chromium in the forms of salts. The former, even in minutest amounts, gives an immediate reaction with diphenyl carbazide, whereas small concentrations of chromium salts do not so react. When chrome mordants are employed in dyeing, the amount used may be about 2 per cent. as dichromate reckoned on the material. After dyeing and washing the whole of this is, in my observation, combined with the fabric and the dye; none is extracted either by water or weak acid solutions at blood heat. In such case it can hardly be supposed to have any physiological activity. Such combined chromium may also be found in silk and some union fabrics containing rayon. Chrome-tanned leathers, such as shoe linings, may contain quite large quantities of total chromium and hat leathers may have small quantities. It is most unusual to find any soluble chromate in such products, but common to find small traces, such as 0·1 per cent., of soluble chromium (expressed as CrO_3) extractable by hot water and a like quantity extractable by weak acid (say 1·0 per cent. acetic acid) at blood heat. If these are the normal occurrence, at what stage is it to be thought that irritant properties arise or that the garment is abnormal? In my view the proper or best extraction media are (*a*) water and (*b*) 1 per cent. acetic acid, or the Society of Dyers and Colourists' acid artificial perspiration liquor,[6] extracting at blood heat.

Metals may be present as necessary mordants or as co-ordination compounds in certain complex dyes, or as a result of after-treatment of the material. Amongst the metals which may be met are antimony, lead, tin, zinc, copper, titanium, nickel and manganese; it is not suggested that these can be considered as irritant, but they need to be determined, if present, and their solubility taken into account. Iron is almost omnipresent as a natural constituent, and aluminium is common in waterproofed garments; most of it is insoluble in water, but much may be extracted with acid. I know of no reason to think that it is harmful. The amount extractable in hot water may be about 0·1 per cent. as aluminium.

In the practical investigation of a specimen it is generally convenient first to determine the acidity, sulphite, mineral matter and any other inorganic constituents and then to proceed to the study of the organic constituents including dyes and intermediates, if any. In considering the organic compounds which may be concerned, having regard to the complexity and variety of modern dyes, I venture to emphasise the importance of the preliminary study of the material and its dyes. Direct application of special tests for individual intermediates is most liable to error and causes subsequent disputes. First, one must observe the nature of the material; this is not always easy with certain rayons. If it is a composite fabric the constituent parts may be examined separately. Then, if there is a pattern, it is well to note whether it results from printing-on with a dye or from weaving of dyed threads; these points are elementary, but they do help in arriving at the truth, for it is only when one has ascertained the nature or grouping of the dyes present that a reliable scheme of testing can be arranged. For example, a cloth dyed with indigo will not contain a diamine, and an acetate rayon will not be in the least likely to contain an amino-phenol. Realisation of such facts would avoid disputes such as have at times arisen. It may be necessary to test for these unlikely substances and if so the interfering dye must first be eliminated. When two or more kinds or colours of fibre are present it is best to examine them separately. In addition to the well-known textbook of A. G. Green, tables prepared by Clayton[7] and by Keyworth[8] are most useful. It is usually impossible to identify all the dyes present, but one should at least ascertain their class or type. Then reference to standard works, such as the Colour Index and Prof. Rowe's recent lectures to the Institute of Chemistry, will give an indication of what intermediates are likely to have been used and what decomposition products of azo-dyes, for example, are possible. A dye formed from, say, benzidine and an amino-naphthol-sulphonic acid will not contain *p*-phenylenediamine.

Next comes an examination of the intermediates, if any are present; they may generally be extracted from the fabric by organic solvents, and some work by Forster and Hanson[9] is very helpful in this direction (*cf.* also Rowe and Levin[10]).

Certain types of rayon are commonly dyed either with amino-anthraquinone derivatives, which appear to dissolve in cellulose esters, or with azoic colours which are based upon aryl amides of β-hydroxy-naphthoic acid, such as naphthol A.S. I have found that free hydroxy-naphthoic acid is sometimes present, possibly as a result of hydrolysis of the amides, and it seems that it is a potential irritant to some people. So far as is known, the anilides or other amides are harmless. These amides are hydrolysed by boiling with acid or alkali, thus



Hence, if an azoic colour is found, it is important to consider what products of hydrolysis, if any, are present; to do this, a quantity of the amide must be hydrolysed and the products separated; it is doubtful whether a certain diagnosis can be made without such work. Many acetate rayons contain small amounts of naphthol A.S. or allied compounds; the quantity may be as much as about 0·2 per cent., though it is usually less. Cotton fabrics may also contain insoluble azo-colours or pigments; these may be separated by dissolving a piece of the material in dilute sulphuric acid and re-crystallising the dye as described by Rowe and Levin,[10] but such procedure should only be used to identify the dye and determine its decomposition products, for it is obvious that it will involve some hydrolysis of the dyestuff. When it has been ascertained what substances are liable to be present it is not difficult to extract any of the free or uncoupled intermediates. Only in such ways is it possible really to determine whether a fabric is normal or whether it contains a supposed irritant.

Another point that is worthy of consideration is the fastness, or otherwise, of the dye in a fabric. There is an increasing number of insoluble vat colours which are dissolved as either leuco compounds or salt complexes of esters and applied so as to form an insoluble dye on both animal and vegetable fibres. If a dye is completely fast and insoluble, it is difficult to see how it can affect the skin. But what if much dye bleeds into water or artificial sweat mixtures? It does not seem reasonable to suppose that a dye is irritant just because it is soluble or will stain the skin. Lipsticks and cosmetics generally contain such colours. Yet one sometimes sees solubility made the basis of some alleged injury. Thus it is important to record the facts, and for this purpose the procedure and reagents proposed by the Society of Dyers and Colourists[6] should be used.

At times certain waterproofed garments have come under suspicion; it may therefore be pointed out that, in addition to aluminium soaps and such waterproofing materials, they are likely to contain mineral pigments such as khaki or iron buffs instead of the familiar synthetic colours. Most garments treated with aluminium soaps or wax compounds yield small quantities of soluble aluminium on extraction, but there is no reason to suppose that such aluminium is irritant. In general, I see no reason why a garment should be alleged to contain an irritant unless it contains something definitely known as such. But it is desirable to obtain and collect reliable data as to what substances and quantities are present; such accumulated information should be valuable in the interests of justice between manufacturers and their customers.

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11, BILLITER SQUARE
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Electrolytic Determination and Separation of Bismuth

Part II. Determinations in Sulphuric and Nitric Acid Solutions

BY F. G. KNY-JONES, M.SC.

METHODS of determining bismuth by electro-analysis in sulphuric acid solution hitherto described have been slow and applicable only to small amounts of the metal.

Hollard and Bertiaux,[1] using a method based on an earlier one of Smith and Knerr,[2] obtained good results for amounts of bismuth not exceeding 0·1 g. in dilute acid solutions, with a current of 0·1 amp. for 48 hours. Scott and Mulligan[3] describe a method for amounts of less than 0·03 g.

Brunck,[4] whose work is quoted in standard analytical textbooks,[5] does not advise the use of sulphuric acid solutions, on the ground that excessive amounts of acid must be added to prevent the formation of basic salts.

Sand,[6] using controlled potential, obtained good deposits of antimony from strongly acid solutions at high temperatures, and was able to effect a rapid separation from tin by this method. By the use of similar conditions for bismuth it has now been found possible to make a rapid determination of that metal in amounts large enough for ordinary analytical work. It should, perhaps, be mentioned that the reason for using controlled potential for this determination is that bismuth generally forms spongy deposits if the electrode potential is not kept as low as possible.[7]

EXPERIMENTAL

DETERMINATION IN SULPHURIC ACID SOLUTION.—Samples of pure bismuth were weighed out and dissolved by heating with 10 ml. of conc. sulphuric acid; in some of the experiments 1 ml. of nitric acid was added to effect more rapid solution of the metal. The solution was cooled and diluted with water, and its volume was adjusted to contain from 20 to 25 ml. of sulphuric acid per 100 ml. One g. of hydrazine sulphate was added as depolariser, and the solution was heated to about 100° C. The electrolysis was carried out at this temperature, with the use of the platinum gauze electrodes, the auxiliary electrode and voltmeter described by Lindsey and Sand.[8]

A saturated calomel auxiliary electrode with a potassium chloride connection was used, the initial potential being 0·055 volt. When the current fell to zero, the auxiliary potential was raised in two or three steps to 0·15 volt and the electrolysis ended when the current fell to zero under this voltage. The deposited metal was washed and dried in the usual manner. Typical results are given in the following table:

Expt. No.	Initial current in amp.	Bismuth taken g.	Bismuth found g.	Temp. ° C.	Time Minutes
1	1·0	0·1323	0·1327	100	15
2	1·2	0·2536	0·2537	105–106	25
3	0·4	0·2009	0·2007	90–105	17
4	0·7	0·1525	0·1525	96–104	10
5	0·4	0·2003	0·1996	95–102	30
6	1·0	0·1298	0·1294	95–100	15
7	0·4	0·1796	0·1795	95–99	20

The deposits obtained were of good appearance and adhered well to the electrode.

DETERMINATION IN NITRIC ACID SOLUTION.—In the course of this work some depositions have been made from nitric acid solutions under the conditions described by Sand[9] and Collin,[10] and the following notes were made:

(1) Small amounts of chlorides (*e.g.* 0·05 g. of potassium chloride) cause precipitation of bismuth oxychloride, and poor, non-adherent deposits of the metal result. By increasing the amount of conc. nitric acid present it is possible to obtain satisfactory deposits, but the presence of chlorides should be avoided.

(2) The deposition can be carried out successfully in the presence of sulphates; hence in the absence of lead, hydrazine sulphate may be used as depolariser instead of the less stable hydrate.

(3) Experiments were made in which the platinum wire described by Brown[11] was used as auxiliary electrode. The method was similar to that described in Part I of this work[12] and, with a P.D. (ΔE) between the cathode and the wire electrode of 0·03 volt rising to 0·1 volt at the end of the electrolysis, good deposits having the correct weight were obtained.

I wish to express my thanks to Dr. H. J. S. Sand for his help and interest.

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Determination of Aluminium by Precipitation with 8-Hydroxy-Quinoline from Mineral Acid Solution; Separation from Large Amounts of Magnesium

BY G. STANLEY SMITH, B.Sc., A.I.C.

THE most rapid method of determining aluminium is undoubtedly by way of its crystalline 8-hydroxyquinoline complex,[1,2] $Al(C_9H_6ON)_3$, which is precipitated within the *p*H range 2·8 to 12·3, the limits for quantitative precipitation being 4·2 and 9·8.[4] The compound is easy to filter off and is practically insoluble in boiling water. It is, however, readily soluble in conc. hydrochloric acid and the solution, after dilution, can be titrated with bromate-bromide solution.

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr.$$

For precipitation in acid solution the published methods[2] describe the addition of an acetic acid solution of the reagent to the warm, slightly acid, aluminium solution previously or afterwards treated with excess of ammonium or sodium acetate. In the present paper another method of obtaining a precipitate is described and put forward as a possible improvement on the older methods, which can yield erratic results. The procedure involves a minimum of manipulation, the results are quantitative, and a sharp separation from a large amount of magnesium is achieved in one operation.

Since magnesium forms a complex which begins to be precipitated if the *p*H rises to slightly over 7, the complete precipitation of aluminium free from magnesium obviously requires close control over the acidity of the solution. After trials of various reagents for automatic control of the acidity the possibility of using a mixture of bromate and bromide, in conjunction with a reagent for removing bromine as soon as it is formed, was investigated.

A bromate-bromide solution was used by Gooch and Osborne[5] in their experiments on the hydrolysis of metallic salts. They obtained practically complete hydrolysis of aluminium sulphate when its aqueous solution was boiled for a long time with bromate-bromide. More recently Moser and Iranyi[6] by similar means reduced the acidity of a hydrochloric acid solution from about 0·1 *N* to 0·002 *N*.

Sodium thiosulphate is stated[7] to react with bromine according to the equation:

$$Na_2S_2O_3 + 8Br + 5H_2O = Na_2SO_4 + 8HBr + H_2SO_4$$

If this equation is considered in relation to that for the reaction between bromate, bromide and acid:

$$5KBr + KBrO_3 + 6HCl = 6KCl + 3H_2O + 6Br,$$

it appears that, in the presence of sufficient bromide, the addition of bromate and thiosulphate to an acid solution in the molecular proportions 4 : 3 should increase the acidity—an effect the opposite of that desired. However, the behaviour of a solution containing a large excess of thiosulphate pointed the way to achieve the end in view. This solution contained, in 500 ml., 60 g. of potassium bromide, 14 g. of potassium bromate and 125 g. of sodium thiosulphate. Tests were carried out as follows:

(1) Ten ml. added to 100 ml. of cold water gave a solution alkaline to methyl red and acid to phenol red, requiring only one drop of 0·1 *N* acid or alkali to change the colours of the indicators. On boiling, the solution became alkaline to phenol red.

(2) Ten ml. added to 100 ml. of boiling water containing 2 ml. of *N* hydrochloric acid remained acid to phenol red on boiling for one minute. On cooling and adding one drop of 0·1 *N* sodium hydroxide, the solution became red (alkaline), but the yellow colour returned on boiling, though the solution remained alkaline to methyl red during a further 15 minutes' boiling, which concluded with the appearance of a cloudiness due to the separation of sulphur.

(3) Ten ml. added to 100 ml. of boiling water containing 7 ml. of *N* hydrochloric acid and boiled for one minute gave a pure yellow colour with methyl red (alkaline), but, on cooling, a pink tinge appeared. Further boiling caused a development of the red colour and, after 5 minutes, the solution became cloudy.

(4) With 6·5 ml. of *N* hydrochloric acid present initially, the solution had to be boiled 3 minutes to give an acid reaction to methyl red.

(5) With 5 ml. of *N* hydrochloric acid the boiling solution was alkaline to methyl red after one minute's boiling, as also after a further 5 minutes.

These results indicate that a solution containing between 2 and 7 ml. of N hydrochloric acid and 10 ml. of the bromate-bromide-thiosulphate solution in 110 ml. will, after boiling for one minute, react alkaline to methyl red and acid to phenol red and, according to the table given by Kolthoff,[8] have a pH between 6·0 and 7·0.

Method.—The following method is suitable for the determination of amounts of aluminium that can conveniently be titrated with 0·1 N bromate-bromide solution:

Reagents.—8-Hydroxyquinoline, 3 per cent. solution in 0·2 N hydrochloric acid; ammonia solution, dilute, approximately 2 N; hydrochloric acid, dilute, approximately N; bromate-bromide-thiosulphate "buffer," as above; bromate-bromide standard solution, 0·1 N (see also below); thiosulphate solution, 0·1 N; 10 per cent. potassium iodide solution; starch solution.

Procedure.—To the slightly acid solution (about 100 ml. in volume, containing up to 0·01 g. of aluminium) add 10 ml. of the hydroxyquinoline reagent, heat to boiling and add dilute ammonia to the well-stirred solution until one drop produces a cloudiness that remains. Add 3 ml. of N hydrochloric acid and boil for a few seconds to give a clear solution. Then add, all at once, to the well-stirred solution 10 ml. of the acidity-regulating solution and boil gently for one minute after boiling begins again. Filter at once through a paper-pulp pad and wash several times with nearly boiling water. Remove the excess of water from the funnel by suction, transfer the pad with forceps to a 500-ml. conical flask, wipe the funnel with a piece of moist filter-paper and put the paper into the flask. Add 30 ml. of conc. hydrochloric acid, shake the flask with a rotatory motion and leave it on a boiling water-bath for two or three minutes to ensure solution of the precipitate. Add 90 ml. of cold water, mix and cool in running water, add a slight excess of the bromate titrating solution, then 10 ml. of 10 per cent. potassium iodide solution, and titrate the iodine liberated by the excess of bromate with thiosulphate (see below).

$$1 \text{ ml. } 0{\cdot}1\ N \text{ bromate} \equiv 0{\cdot}0002248 \text{ g. aluminium.}$$

For amounts of aluminium less than 5 mg. the presence of 5 to 10 g. of ammonium chloride is to be recommended, and the process is slightly modified as follows:—To the solution containing ammonium chloride add a few drops of methyl red indicator (non-alcoholic) and then dilute ammonia carefully until the indicator changes colour. This is followed by 10 ml. of the hydroxyquinoline reagent, 1 to 2 ml. of N hydrochloric acid and, after boiling to produce a clear solution, 10 ml. of the "buffer" solution.

Titration.—An accurate direct titration with bromate is impossible, but methyl red or indigo-carmine can be used as internal indicator to show when an excess of bromate has been added. Since the indicator is gradually oxidised during the addition of bromate, it is usually necessary to introduce from time to time further quantities of the indicator. This is troublesome, and for accurate work a correction has to be applied.

I have found that the indicator (indigo-carmine) may, with advantage, be dissolved in the bromate solution. The correction, once determined, is then valid for all future titrations, as it is exactly proportional to the volume of bromate used and appears in the calculation only as a constant factor for the solution. A suitable quantity is 25 ml. of 0·5 per cent. aqueous indigo-carmine in 1 litre of 0·1 *N* bromate-bromide solution, the factor of which will be reduced by about 0·75 per cent. A solution containing in 1 litre 2·805 g. of potassium bromate, 12 g. of potassium bromide and 25 ml. of 0·5 per cent. indigo-carmine solution will probably be exactly 0·1 *N*. If the amount of potassium bromide is doubled, much of the indicator is thrown out of solution on standing. It should be mentioned that the bromate solution containing indigo-carmine must be used for titrating cold solutions only.

During a titration with this solution the hydroxyquinoline solution soon becomes deep green, and it remains green until, in the neighbourhood of the end-point, it tends to yellowish-green. If the bromate is then added slowly to the well-agitated solution, there appears, 1 to 3 ml. past the calculated end-point, a yellow colour nearly free from green. Potassium iodide may then be added at once and the iodine titrated with thiosulphate, starch solution being used. The end-point is very sharp, the final colour being a greenish-yellow.

The use of carbon disulphide[9] before the thiosulphate titration, besides being unpleasant, is quite unnecessary,[3] and may very well be abandoned. If the acidity after the addition of bromate is 2 to 3 *N*, no trouble is likely to arise.

The results shown in the table were obtained by the method described above. The aluminium taken was in the form of a solution of pure aluminium in hydrochloric acid or of aluminium ammonium sulphate. In each test the volume before addition of 10 ml. of the buffer solution was 100 to 110 ml., and the solution contained 10 ml. of 3 per cent. hydroxyquinoline together with any ammonium chloride or magnesium, as chloride or sulphate, in the amounts shown.

Aluminium mg.	Ammonium chloride g.	Magnesium g.	Titration, 0·1 *N* bromate required ml.	Calculated titre ml.
10·00	—	—	44·5; 44·6	44·5
10·00	6	0·3	44·6; 44·65	44·5
7·50	—	—	33·4; 33·5; 33·5	33·4
7·50	6	—	33·45	33·4
7·50	6	0·8	33·6	33·4
7·50	6 (also 1 g. of tartaric acid)	0·8	33·4	33·4
7·50	do.	—	33·45	33·4
5·00	—	—	22·25; 22·25	22·25
5·00	—	1·0	22·25; 22·25	22·25
5·00	—	5·0	22·5	22·25
2·50	—	—	10·6; 10·9	11·1
2·50	10	—	11·05; 11·1	11·1
1·25	—	—	5·0; 5·1	5·55
1·25	10	—	5·5	5·55
0·50	10	—	2·15	2·2

The solution employed for regulating the acidity in the precipitation of aluminium with hydroxyquinoline should also be applicable to the precipitation of aluminium hydroxide in presence of manganese and magnesium. The *p*H for the precipitation of the hydroxides of the latter metals could never be attained, even locally.

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April 28th, 1939

First Report of the Poisons Sub-Committee appointed to investigate Methods of Assay for Various Substances appearing in the Poisons Schedules of the Poisons Regulations, 1935, to the Analytical Methods Committee of the Society of Public Analysts and other Analytical Chemists

I. ASSAY OF LOBELIA (*LOBELIA INFLATA*)

MEMBERS OF THE SUB-COMMITTEE.—G. Roche Lynch, O.B.E., M.B., B.S., F.I.C. (*Chairman*); N. L. Allport, F.I.C.; C. E. Corfield, B.Sc., F.I.C.; C. Edwards, B.Sc., F.I.C.; D. C. Garratt, B.Sc., Ph.D., F.I.C.; C. H. Hampshire, M.B., B.S., B.Sc., F.I.C.; W. H. Linnell, M.Sc., Ph.D., F.I.C.; W. A. N. Markwell, A.I.C.; J. R. Nicholls, B.Sc., F.I.C.; A. D. Powell, F.I.C.; A. I. Robinson, Ph.C.; C. E. Sage, F.I.C.; Norman Evers, B.Sc., F.I.C. (*Hon. Secretary*).

SURVEY OF METHODS.—The most important methods previously published for the assay of lobelia are as follows:

Vanderkleed and E'We (*J. Amer. Pharm. Assoc.*, 1916, **5**, 713).
Wieland (*Ber.*, 1921, **54**, 1784).
Mascre (*Bull. Sci. Pharm.*, 1930, **37**, 209).
Peyer and Gstirner (*Arch. Pharm.*, 1932, **270**, 44).
Markwell (*Pharm. J.*, 1936, **136**, 617).

The methods of Vanderkleed and E'We and of Mascre were tried and compared with that of Markwell. The last method was found to be the most satisfactory in working and to give the most uniform results. The Sub-committee decided to concentrate on Markwell's method, and a sample was circulated on which the method as published was carried out. The results were as follows:

Member	Alkaloids as lobeline by titration Per Cent.	 by weighing Per Cent.
A	0·51	—
	0·52	—
	0·51	—
B	0·43	—
C	0·51	0·62
	0·49	0·63
	0·51	0·57
D	0·45	—
	0·46	—
E	0·44	—
	0·43	—

The results of three of the workers were clearly lower than those of the other two. It was suggested that the quantity of ammonia added to precipitate the alkaloid might have some effect on the result. Comparative tests were therefore carried out (*a*) adding a slight excess of ammonia, and (*b*) adding 5 ml. of dilute ammonia in excess. Alternative methods of effecting solution of the alkaloidal residue in standard acid were also tried, *viz.* (*a*) dissolving in 2 ml. of absolute alcohol before adding the standard acid, and (*b*) dissolving the residue in chloroform and boiling off the chloroform in the presence of the standard acid. The results of these further tests on the same sample were as follows:

Member	Conditions	Alkaloids by titration Per Cent.	 by weighing Per Cent.
A	Slight excess of ammonia	0·49	—
	,, ,, ,, ,,	0·51	—
	5 ml. ,, ,, ,,	0·51	—
	Residue dissolved in alcohol	0·49	—
B	Slight excess of ammonia	0·48	—
	Residue dissolved in alcohol	0·48	—
C	Slight excess of ammonia	0·47	0·60
	5 ml. ,, ,, ,,	0·49	0·61
	Residue dissolved in alcohol	0·50	0·62
	,, ,, ,, chloroform	0·49	0·62
D	Slight excess of ammonia	0·46	—
	5 ml. ,, ,, ,,	0·48	—

As far as these results are significant, it appears that the results are slightly higher when an excess of ammonia is added. The method of dissolving the residue does not seem to have any effect. It is considered that these results are sufficiently satisfactory to recommend the method for adoption.

RECOMMENDED METHOD.—Introduce 10 g. of the lobelia in No. 60 powder and 10 g. of ignited sand into a pear-shaped separating funnel provided with a plug of cotton wool in the tube below the stopcock. Add 75 ml. of a mixture of 4 vols. of ether and 1 vol. of 95 per cent. alcohol (by volume). Shake and set aside for 15 minutes, add 5 ml. of dilute ammonia (10 per cent. of NH_3) and shake in a mechanical shaker for 1 hour or by hand for 1 minute at 10-minute intervals during 1 hour. Allow the liquid to percolate into another separating funnel. When the liquid ceases to flow, pack the drug firmly by means of a button-ended glass rod. Continue the percolation, first with 25 ml. of the ether-alcohol mixture and then with ether, until the alkaloid is completely extracted, as shown by testing in the usual manner.

To the percolate add 30 ml. of *N* sulphuric acid.* Shake well and allow to separate. Run off the lower layer into another separator. Repeat the extraction with a mixture of 25 ml. of 0·5 *N* sulphuric acid with 5 ml. of alcohol (95 per cent.). Run off the lower layer and repeat with three further quantities of 20 ml. of the acid-alcohol mixture or until the alkaloids are completely extracted. Wash the mixed acid solutions, first with 10 ml. and then with successive quantities of 5 ml. of chloroform, washing each chloroformic solution with the same 20 ml. of 0·5 *N* sulphuric acid contained in another separator. Reject the chloroform, transfer the acid liquid from the second separator to the first separator, neutralise to litmus with dilute ammonia solution and add a further 5 ml. in excess.

Extract the alkaloids by shaking with successive quantities of 10 ml. of chloroform. Combine the chloroform solutions and wash with 3 ml. of distilled water. Filter the chloroform solution through a 7-cm. filter paper into a flask. Wash the filter thoroughly with more chloroform and collect the washings in the flask. Distil the chloroform from a water-bath until about 2 ml. remain. Add 2 ml. of absolute alcohol and continue the evaporation on the water-bath, using a gentle air-blast to complete the process. Repeat with two further lots of absolute alcohol to ensure dehydration of the residue. Heat the residue for 1 hour at 80° C.

Add to the residue 2 ml. of alcohol (95 per cent.) and warm until dissolved. Add 10 ml. of 0·02 *N* sulphuric acid. Cool and titrate with 0·02 *N* sodium hydroxide or sodium borate solution, using methyl red as indicator. One ml. of 0·02 *N* sulphuric acid is equivalent to 0·00674 g. of the alkaloids of lobelia calculated as lobeline.

A further sample of the drug was circulated, and the recommended method was compared with the methods of the French Codex (6th edition) and of the Swiss Pharmacopoeia (5th edition).

The results are set out in the following table:

	Lobeline on the undried drug		
Member	Recommended method Per Cent.	French Codex Per Cent.	Swiss Pharmacopoeia Per Cent.
A	0·351	0·345	0·405
	0·344	0·320	0·337
B	0·330	0·362	0·318
	0·320	0·342	0·320
	0·320	—	0·300
C	0·35	0·41	—

It was agreed that the recommended method gave more consistent results and is less open to objection than either of the two pharmacopoeial methods.

The experimental work reported in the tables was carried out by an appointed panel which had also the assistance of Mr. G. R. Page, of the British Pharmacopoeia Commission's Laboratory, in carrying out some of the analyses.

(*Signed*) G. ROCHE LYNCH (*Chairman*)
NORMAN EVERS (*Hon. Sec.*)

June, 1939

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* It is important that hydrochloric acid should not be used, since lobeline hydrochloride is soluble in chloroform.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

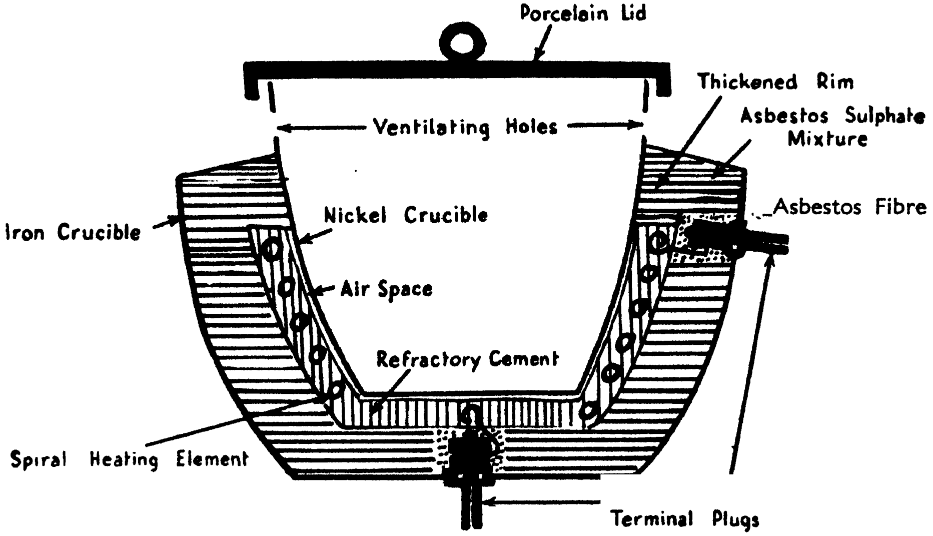
A SIMPLE ELECTRICAL APPARATUS FOR HEATING SINGLE CRUCIBLES

INCINERATION is a procedure frequently employed in biochemical research. Electrical or gas muffle furnaces as at present available are heavy, clumsy and expensive, and inability to control temperature to any degree of accuracy renders incineration by ordinary gas-burners unsatisfactory. For these reasons an economical, small, electrically heated furnace has been evolved which may be cheaply and easily constructed. The furnace holds one crucible and can be so designed that the internal temperature can be fixed at a predetermined level or varied to suit the operator's requirements.

The materials required for one furnace are:—(1) An iron crucible 5 in. (12·5 cm.) top diameter and 3 in. (7·5 cm.) deep. (2) A nickel crucible 3 in. (7·5 cm.) top diameter and 3 in. (7·5 cm.) deep. (3) Nickel-chrome resistance wire, 26 s.w.g., about 6 ohms/yard ("Brightray," Messrs. H. Wiggin & Co., Birmingham). (4) Two mica-insulated terminal plugs. (5) Two socket connectors to fit (4). (6) Asbestos wool, about ¾ lb. (330 g.). (7) Calcium sulphate (plaster of Paris) about ¼ lb. (110 g.). (8) Refractory cement about ½ lb. (220 g.) ("Pyruma," Messrs. J. H. Sankey, London). The furnace is constructed in the following way:—Make a dry mixture of the asbestos and the calcium sulphate and knead about three quarters of it with water to the consistence of dough. Next take the iron crucible and press into it enough of the wet mixture to cover the bottom to a depth of ⅜ in. (0·93 cm.), leaving a bare circular patch 1 in. (2·5 cm.) in diameter in the centre of the bottom. On this layer place a mould of the same shape as the iron crucible but with a top diameter of 3½ in. (8·5 cm.). A small iron crucible makes a suitable mould. Pack the space between the mould and the crucible with the asbestos-sulphate mixture to within ¼ in. (0·6 cm.) of the top of the crucible, leaving another bare area 1 in. (2·5 cm.) in diameter 1 in. (2·5 cm.) from the rim. As soon as the packing has had time to harden a little the mould may be removed and the lining allowed to dry out. Drill holes ¼ in. (0·6 cm.) in diameter in the centre of the two areas of uncovered metal. These are for the terminal plugs.

It is necessary at this stage to take into account the work that the finished apparatus will be required to do. If it is to be used for a purpose requiring a fixed temperature it is necessary to arrange the resistance of the heating element accordingly (see below). If the apparatus is to be used at more than one temperature, one of several alternative arrangements may be employed. The most economical of these is to construct two furnaces and to connect them in series across the mains so that the temperature produced is the lowest at which ashing is likely to be carried out. This allows subsequent alterations of temperature by re-arrangement of the connections and addition of a suitable rheostat. Another method is to make one furnace only and use it with a rheostat in series. This last method is rather wasteful, because power is unavoidably lost in heating the rheostat. Also, the rheostat alone costs as much as the furnace itself.

If one apparatus only is required to work at a fixed temperature which will be high enough to give complete oxidation of carbon without loss of potassium or other relatively volatile elements, that is, approximately 450° C., the total resistance of the windings should be about 100 ohms at 220 volts, and the heating element will accordingly consist of 15 to 18 yards (metres) of the nickel-chrome resistance wire. If two furnaces are to be made and used for ashing at 450° C. they should each have a resistance of about 45 ohms at 220 volts and be connected in series. If a higher temperature is required, the two can be disconnected and either of them connected in series with a rheostat, which should have a total resistance of 50 ohms, and be capable of carrying 5 amps. at 220 volts.



Having decided on the most suitable arrangement, measure off the required length of wire and wind it on a rod into a close spiral of about 3/16 in. (0·5 cm.) diameter. When all the wire is wound, draw out the spiral to a length of about 3 feet (1 metre). Straighten both ends of the wire for a distance of 1 in. (2·5 cm.). Then wet thoroughly the inner surface of the asbestos and apply a layer of refractory cement about $\frac{1}{8}$ in. (0·3 cm.) thick. Pass one end of the spiral of wire through the hole in the bottom of the crucible, fix it with a cork and then partly embed the wire in the refractory cement in a regular spiral formation. Pass the other end of the wire through the hole near the rim of the crucible and secure it with another cork. Allow the whole crucible and its contents to dry in an oven at 100° C. When dry, insert the mica-insulated plugs into their holes and fasten down the securing nuts. Connect the ends of the resistance wire with their respective terminals and screw down the locking nuts to hold the wire. Fill in the space around the nuts with wet asbestos fibre until level with the inner wall of refractory cement. This soft filling facilitates subsequent removal of the wire should it become necessary. Now cover the whole inner surface of the crucible and the coils of wire with a layer of refractory cement. The total thickness of cement will now be about $\frac{1}{4}$ in. (0·6 cm.); the coils of wire should be just covered and the inner surface smooth.

Drill 9 holes, $\frac{1}{4}$ in. (0·6 cm.) in diameter, in a ring $\frac{1}{2}$ in. (1·2 cm.) from the rim of the nickel crucible and place the nickel crucible inside the asbestos-lined iron crucible so that it clears the refractory lining by about $\frac{1}{8}$ in. (0·3 cm.) both from sides and bottom (see sectional diagram). It may be held off the bottom at this stage by a small piece of packing material. Then fill the space between the two crucibles above the embedded heating element with the same asbestos-sulphate mixture as was used for the preliminary lining. The position and shape of this thickened rim can be seen from the diagram. As soon as the rim has set take out the nickel crucible and remove the temporary packing piece. When the whole is thoroughly dry replace the nickel crucible, which should now be held firmly by the thickened upper rim.

The furnace may conveniently be mounted in a 5½ in. (14 cm.) ring clamped on a retort stand. When in place plug in the socket connectors fitted to 5-amp. asbestos flex and cover the nickel crucible with a porcelain lid 3½ in. (8·75 cm.) in diameter. The furnace is now ready for testing. This should be done under working conditions with a 500° C. thermometer. If necessary, the temperature may be reduced by means of a small external resistance, consisting of a few turns of resistance wire wound on a piece of uralite. The material to be ashed is put into a silica or platinum crucible within the furnace. The apparatus will be found to ash satisfactorily at any temperature between 400 and 450° C., and the time taken to oxidise all the carbon will vary from 1 to 36 hours, depending on the type of material being incinerated.

It is clear that this apparatus has many applications other than that for which it was originally designed (dry ashing at 450° C.). Thus it may be used as a heating unit for distilling small quantities of liquids, and for this purpose the nickel crucible can be partly filled with a liquid of suitable boiling-point, with sand or with flake asbestos, or may be removed entirely. The apparatus may also be useful in the determination of melting-points. Units that were constructed to run at a temperature of 450° C. on a 200-volt supply have been found to make excellent heaters for Soxhlet extractions (ether). For this purpose the nickel crucibles were removed and the terminals were connected with a 100-volt source of current.

Furnaces as used in this department may be obtained from the Scientific Glassblowing Co., Ltd., London.

SUMMARY.—The construction of a simple inexpensive apparatus is described for dry ashing at 450° C. Simple modifications allow the temperature to be varied to suit other requirements and in this way the apparatus may be used for other purposes.

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MOHLER'S TEST FOR BENZOIC ACID

A DISADVANTAGE of Mohler's test, described in THE ANALYST (1932, **57**, 224) is the rapid fading, on dilution, of the colour due to *m*-diamino-benzoic acid. It has recently been discovered that if the dilution is made with the solution prepared as described below, the colour does not fade and the mixture may be diluted at will.

Preparation.—Twenty ml. of conc. sulphuric acid are added to 40 ml. of water containing 2 g. of potassium nitrate, and the liquid is cooled while 200 ml. of water containing 100 ml. of ammonia (sp.gr. 0·880) are carefully added. Finally, 40 ml. of water, in which 0·8 g. of hydroxylamine hydrochloride is dissolved, are added to the solution.

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THE DETERMINATION OF MANGANESE, ESPECIALLY IN BIOLOGICAL MATERIAL

OXIDATION of manganese by means of periodate has been found satisfactory for the determination of the metal in a wide variety of materials; according to the amount of manganese present, the determination may be completed colorimetrically or volumetrically. The process is carried out in a hot mixture of phosphoric and sulphuric acids. (*Cf.* Willard and Greathouse, *J. Amer. Chem. Soc.*, 1917, **39**, 2366; Abst., ANALYST, 1918, **43**, 44; Richards, ANALYST, 1930, **55**, 554.) For quantities of manganese between 0·1 and 1·0 mg. it has been found possible to measure photoelectrically the permanganic acid formed. The instrument we have used is the Hilger Spekker Absorptiometer. The excess of the oxidising agent in the reaction mixture stabilises the permanganate formed, so that the solution is suitable for colorimetric measurement. With lead peroxide or sodium bismuthate as oxidising agent, this advantage is not present.

We have found the method to be satisfactory for the determination of manganese in biological material after it has been ashed. With pharmaceutical products containing large amounts of iron the method also works well; the procedure is to destroy the organic matter by ignition, to fuse the residue with potassium bisulphate, and to oxidise the manganese; excellent results have been consistently obtained. Appreciable amounts of manganese have been found in a number of commercial samples of iron salts, as shown below:

Ferrous sulphate (AnalaR)	100 p.p.m.
Exsiccated ferrous sulphate (Coml.) ..	700 „
Iron ammonium citrate (scales B.P.) ..	300 „

When the quantities of manganese lie between 10 and 30 mg. we use a slight modification of the volumetric method put forward by Willard and Thompson (*Ind. Eng. Chem., Anal. Ed.*, 1931, 399; Abst., ANALYST, 1931, 56, 830). The excess of periodate, after completion of the oxidation, is precipitated with mercuric nitrate; the reaction mixture is filtered into a known amount of ferrous sulphate solution, sufficient to furnish an excess that can be determined with permanganate. Willard and Thompson used "$Hg(NO_3)_2 2H_2O$ dissolved in a little water" for precipitating excess of periodate. We examined two samples of mercuric nitrate (obtained in this country) and found them to be basic and only partly soluble in water. We therefore dissolved the requisite amount for precipitation in the minimum necessary quantity of dilute nitric acid, and oxidised this solution with just sufficient permanganate; it was then ready for use as a precipitant. We found that asbestos, recommended for the filtration by Willard and Thompson, caused a small loss of manganese, and were able successfully to replace it by a layer of kieselguhr ("Hyflo Supercel"). We have also found that it is possible to carry out the oxidation in dilute sulphuric acid (5 per cent. w/v) without any phosphoric acid being present, and that this does not lead to trouble from precipitation of manganese oxides. We have applied the method to manganese sulphate, to manganese butyrate after removal of butyric acid by evaporation with sulphuric acid, and to manganese glycerophosphate after ignition. We have found that the B.P.C. method for assaying manganese glycerophosphate by ignition to pyrophosphate may give misleading results; commercial samples apparently contain from 1 to 3 per cent. of calcium, and this is calculated as manganese in assays by the B.P.C. method. It is better to dissolve the ash, after ignition, in dilute sulphuric acid, and to determine the manganese by the method of Willard and Thompson.

In attempting to determine manganese in manganese sulphate by precipitation as manganese ammonium phosphate, we obtained variable results. Satisfactory results, on the other hand, were obtained by the method of Volhard (Treadwell and Hall, 4th Ed., Vol. II, p. 612), in which manganous manganese is titrated with potassium permanganate in hot solution in presence of zinc sulphate. The end-point of this method, however, is difficult to ascertain, owing to the presence of a brown precipitate of zinc manganite.

I would like to express my thanks to Mr. A. F. Lerrigo for his advice and criticism of the work that forms the basis of this note, and to the Directors of Glaxo Laboratories, Ltd., in whose Analytical Department it was carried out, for permission to publish the results.

F. E. READ

GLAXO LABORATORIES, LTD.
GREENFORD, MIDDLESEX

June 21st, 1939

NOTES ON THE VOLUMETRIC IODIDE METHOD[1] OF DETERMINING STARCH

THE convenience and rapidity of centrifugal methods in the separation of interfering substances is shown in the following description of the analysis of cocoa. The starch in one sample can be determined in 1¼ hours and the only multiplication of apparatus needed for the completion of 20 samples in a day is that of the centrifuge tube. The method is capable of general application to starch-containing substances and may usually be shortened. Thus there is no need for a preliminary separation of sugar with diluted alcohol unless it is present in sufficient quantity to produce large amounts of caramel when heated with alcoholic potassium hydroxide; the heating with alcoholic potassium hydroxide can be omitted when only small amounts of fat and protein are present; it is unnecessary to re-precipitate the starch with 40 per cent. alcohol and wash with $N/5$ potassium acetate solution in the absence of dextrin, and the results for starch are within 0·1 per cent. if this is omitted in chocolate analysis. The presence of colouring matter, tannin and other substances in cocoa, which are precipitated if an attempt is made to neutralise the solution, before adding iodine to precipitate the starch, renders a preliminary separation necessary so that these substances can be removed by decantation and washing before the final titration for starch, and this is best done by adding iodine to the aqueous potassium hydroxide solution. If quantities larger than 0·5 g. of cocoa are used the decanted solution should be tested to see that it contains an excess of iodine.

The presence of fibre in cocoa facilitates the clarification of the various solutions, which can be decanted without filtration. A volumetric measure of the fibre is obtained if, after acidifying the final titrated starch and fibre mixture (with 3 ml. of conc. hydrochloric acid), the tube is heated in a boiling water-bath and then whirled; after the clear liquid has been decanted the fibre can be washed in the centrifuge tube, transferred to a platinum dish, dried and weighed. Whirled for 5 minutes at a speed of 1000 r.p.m., 1 ml. of apparent fibre = approx. 0·02 g. of dried fibre.

In my opinion the determination of starch means the determination of the amylo group, whether it is present as amylose, amylopectin or amylo-hemicellulose, but the last of these may be approximately estimated by adding taka-diastase to the gelatinised mixture at pH 7 and incubating at 38° C. for 1 hour; the amylose and amylopectin are transformed into sugar, leaving the insoluble amylohemicellulose, the amylo group of which can then be determined by the iodide method.

STARCH IN COCOA.—The preliminary treatment for the removal of interfering substances yields a mixture of starch and fibre; the starch is then determined by the volumetric iodide method.

(*a*) *Removal of fat and protein.*—Weigh 0·5 g. of cocoa into a 50-ml. centrifuge tube, add 30 ml. of an 8 per cent. alcoholic solution of potassium hydroxide and heat (with stirring) for 5 minutes in a water-bath at 80° C.; dilute the mixture to 50 ml. with industrial spirit and whirl in a centrifuge; decant the clear liquid and wash the residue once with hot industrial spirit, whirl and decant the clear liquid.

(*b*) *Preparation of starch solution.*—To the residue from (*a*) add 20 ml. of a 0·7 per cent. aqueous solution of potassium hydroxide and heat (with stirring) for 10 minutes in a water-bath at 95 to 100° C.; dilute the mixture to 40 ml. with water and cool.

(*c*) *Initial precipitation of starch to remove colouring matter, etc.*—To the starch solution from (*b*) add 4 ml. of N iodine solution and adjust to 50 ml. with approximately 2 N potassium acetate solution, cork the tube, shake, whirl and decant the clear liquid; wash the residue once with approximately $N/5$ potassium acetate solution and 1 ml. of $N/10$ iodine solution, cork the tube, shake, whirl and decant the clear liquid.

(*d*) *Re-precipitation of starch iodide.*—To the residue from (*c*) add 2 ml. of *N*/10 sodium thiosulphate solution (to reduce the iodide and re-dissolve the starch), dilute the mixture to 28 ml. with water, add 2 ml. of *N*/10 iodine solution and 20 ml. of industrial spirit, cork the tube, shake, whirl and decant the clear liquid; wash the residue once with approx. *N*/5 potassium acetate solution and 1 ml. of *N*/10 iodine solution, cork the tube, shake, whirl and decant the clear liquid.

(*e*) *Volumetric determination of starch.*—To the residue from (*d*) add 1 ml. of *N*/10 sodium thiosulphate solution to dissolve the starch, dilute to 40 ml. with water, add 4·5 ml. of *N*/10 iodine solution followed by 5 ml. of approx. 2 *N* potassium acetate solution, make up to 50 ml. with water, cork the tube, shake and whirl for 10 minutes. Pipette off 25 ml. of the clear liquid and titrate with *N*/100 sodium thiosulphate solution; titrate the remaining liquid together with the precipitate with *N*/100 sodium thiosulphate solution, and calculate the starch.

STARCH IN SWEETENED CHOCOLATE.—(i) *Removal of sugar.*—Weigh 2 g. of chocolate into a 50-ml. centrifuge tube, add 15 ml. of hot water and, after stirring to dissolve the sugar, add industrial spirit and 1 ml. of *N* iodine solution to the 50-ml. mark; cork the tube, shake, whirl and decant the clear liquid; wash the residue once with 70 per cent. industrial spirit, cork the tube, shake, whirl and decant the clear liquid.

(ii) *Determination of starch.*—To the residue add 30 ml. of an 8 per cent. alcoholic solution of potassium hydroxide and proceed as for cocoa.

RESULTS.—The following results were obtained:

	Starch in original substance Per Cent.	Starch in fat-free and sucrose-free dry substance Per Cent.
Cocoa A	11·0	15·0
,, B	11·2	16·0
,, C	12·7	17·5
,, D	13·0	18·0
Chocolate E ..	2·2	16·0
,, F ..	2·3	16·0
,, G ..	2·5	16·5
,, H ..	2·9	17·0

The fat was extracted from Cocoa C, the fat-free substance was dried, and the sample was well mixed. Four 0·5-g. samples were weighed into centrifuge tubes, and the analysis was carried out as described. The titrated mixtures of starch and fibre were acidified with 3 ml. of conc. hydrochloric acid, and the tubes were placed in a boiling water-bath for 30 minutes and then whirled; after the acid liquid had been decanted, the fibre was washed twice with water, transferred to a platinum dish, dried and weighed and ignited, and the ash was weighed.

The following results were obtained:

Number of test	Weight of fat-free dried substance g.	Starch found by volumetric iodide method Per Cent.	Apparent volume of fibre ml.	Weight of dried fibre g.	Weight of ash in dried fibre g.	Fibre Per Cent.
1	0·5	17·6	1·4	0·031	0·002	5·8
2	0·5	17·5	1·4	0·032	0·002	6·0
3	0·5	17·5	1·4	0·032	0·002	6·0
4	0·5	17·4	1·4	0·031	0·002	5·8
Average	0·5	17·5	1·4	0·0315	0·002	5·9

Fibre determined by the usual method of digesting the dry fat-free material with dilute sulphuric acid and then with alkali:

	2·0	—	—	0·119	0·003	5·8

The taka-diastase method was applied to the titrated starch and fibre mixtures. Five ml. of a 1 per cent. solution of taka-diastase were added to each tube, the *p*H was adjusted to 4 with sodium acetate and acetic acid buffer, including that of the blank, the tubes were incubated at 38° C. for 36 hours, and the resulting sugars were determined by the ferricyanide and iodine method; the polarimetric and copper reduction method was also used, by re-precipitating the starch from a number of titrated solutions and collecting the starch and fibre into one tube so as to obtain a larger reading on the polarimeter. The starch found by both methods was within 0·5 per cent. of that determined by the iodide method. The average amount of starch in the fat-free dried substance of cocoa, found by the usual taka-diastase method, is about 14 per cent.

The explanation of this low result with the taka-diastase method probably lies in the fact that insoluble compounds of starch, such as amylo-hemicellulose, are only slowly acted on by taka-diastase at a *p*H above 6. On applying the iodide method to the insoluble residue left after the usual taka-diastase action on the fat-free dried substance had proceeded for 24 hours, it was found that 1·5 per cent. of starch remained in the residue, and a duplicate test after 48 hours' incubation showed that 0·5 per cent. remained in the residue. Similar results are obtained with some cereals unless the *p*H is adjusted to 4 or 5. If the *p*H is adjusted to 4 with a buffer of sodium acetate and acetic acid the addition of toluene is unnecessary.

It has been found that the following table of factors applies to all quantities of starch if 4·5 ml. of $N/10$ iodine solution (containing 0·25 g. of potassium iodide) and 5 ml. of 2 N potassium acetate solution of *p*H 6·4 (adjusted with acetic acid) are used in the test:

$N/10$ iodine in excess in 50 ml. ml.		Starch g.
4·0	1 ml. of $N/100$ sodium thiosulphate =	0·00555
3·5		0·00561
3·0		0·00571
2·5		0·00582
2·0		0·00592
1·0		0·00643

REFERENCE

1. W. Whale, ANALYST, 1938, **63**, 328, 421.*

W. WHALE

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June 1*st*, 1939

ASSAY OF BELLADONNA ROOT AND ITS PREPARATIONS

The B.P. method for the assay of belladonna root does not work satisfactorily with "Atropa Belladonna" obtained from Kashmir. On account of the abnormally large amount of resins and red colouring matter found in these roots (which consist mostly of the "crowns" rather than the longitudinal stems of the roots) as compared with the official roots, the final alkaloidal residue is so highly coloured that it is impossible to titrate it accurately. The same difficulty is experienced in the assay of preparations from these roots.

* Copies of this reprint may be obtained on application to the author.

Gum tragacanth has been found by a number of workers to eliminate most of the troublesome resins and colouring matter which interfere with the assay of alkaloidal drugs; I have found that the use of gum tragacanth gives excellent results in the assay of belladonna root and its preparations. The actual manipulation is as follows:

ASSAY OF BELLADONNA ROOT.—The alkaloids are liberated and extracted with ether and alcohol as described in the B.P. Very often about 400 to 600 ml. of percolate is obtained for every 10 g. of root powder, and this may advantageously be partly concentrated over a warm water-bath. After cooling, 1·0 g. of gum tragacanth powder and 2 to 3 ml. of water are added to the percolate and thoroughly shaken for about five minutes. The gum coagulates readily, removing most of the resins and colouring matter from the alkaloidal solution. The solution is allowed to stand for about five minutes—when it will be clear—and filtered into a separating funnel through a tight plug of cotton wool, the flask and the residue being washed with small portions of ether until the alkaloids have been completely transferred to the separator. The assay is then continued with this solution, as described in the B.P., but with the use of dilute hydrochloric acid instead of sulphuric acid for extraction.

ASSAY OF PREPARATIONS FROM BELLADONNA ROOT.—Ten ml. of liquid extract (or corresponding quantities of other preparations) are mixed with 1·0 g. of tragacanth powder and 1·5 to 2·0 ml. of dilute solution of ammonia are added. The mixture is thoroughly stirred with a glass rod until the gum coagulates. The alkaloids are completely extracted with ether by kneading the coagulated mass in the solvent, each portion of ether being filtered into a separator through a tight plug of cotton-wool. The assay is then carried out as indicated above.

The advantages of this modified procedure are:

1. The formation of troublesome emulsions is completely avoided and the extractions can be carried out more quickly. The assay can be completed in about 8 or 9 hours, whereas the B.P. method requires 12 to 14 hours.
2. The final alkaloidal residue is obtained as a light brown, transparent mass giving a colourless or very pale yellow solution in sulphuric acid which can be titrated much more easily and accurately than the deep reddish solution obtained by the B.P. method.
3. The method can be applied to all commercial grades of "Atropa Belladonna," even those that contain unusually large proportions of resins and colouring matter.

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June 24th, 1939

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1939

OF the 1541 samples submitted under the Food and Drugs Act, 1475 were bought informally.

FORMALIN TABLETS WITHOUT FORMALIN.—Three samples were returned as incorrect. According to the B.P. Codex each tablet should contain 9·7 mg. of paraformaldehyde together with citric acid, menthol and a little oil of lemon. The first sample consisted of three different kinds of tablets: about 20 large tablets containing no formalin at all, three small opaque tablets, which also contained no formalin, and three small translucent tablets, each of which contained 4 mg. of paraformaldehyde. The vendor was aware that there were three different kinds, but had bought them in good faith from a reputable firm. This firm stated that the tablets they supplied were not of B.P.C. strength, but should have contained 4·7 mg. of paraformaldehyde per tablet; in future all their tablets would be made to the B.P.C. standard.

The second sample contained only 4 mg. of paraformaldehyde per tablet. The wholesale dealer collected the whole stock and destroyed it. The third sample contained only 2 mg. of paraformaldehyde per tablet. In this case the wholesale dealers, replying to the vendor, said that, whilst there was a deficiency of formalin, the tablets sent to them were a mixed lot and some were not of their manufacture. They also alleged that it was difficult to guarantee that the full amount of formalin would be retained over a prolonged period unless the tablets were kept in completely air-tight containers and not exposed to warmth. The retailers advised all their branches to carry very small stocks and to exercise special care in storage. Tests applied to the stock of tablets at headquarters showed them to be of full strength. H. H. BAGNALL

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1938

OF the 1284 samples examined, 396 were bought formally.

CHESHIRE CHEESE.—A sample purchased as "full cream Cheshire cheese" was found to contain 29·0 per cent. of fat and 44·8 per cent. of moisture (= 52·5 per cent. of fat on the dry substance). Enquiries by the sampling officer showed that the sample was a full cream cheese of Dutch origin. As there is no Marking Order under the Merchandise Marks Act, 1926, requiring cheese to be labelled, and as it is acknowledged that Cheshire type cheese can be manufactured outside this country, and, further, since the sample conformed to the standard of 45 per cent. of fat on the dry cheese, no action could be taken against the vendor. The Cheshire Cheese Federation propose to take joint action with other British cheese interests with a view to applying for a Marking Order.

POTASSIUM IODIDE METHOD OF MEASURING SOLAR RADIATIONS.—This process has been in continuous use for 12 years at four stations (*cf.* ANALYST, 1933, **58**, 690; 1937, **62**, 667). The solar radiation is expressed as milligrams of iodine liberated by an exposure from 9 a.m. to 9 a.m. The totals for 1938 and the yearly averages for 5 years were as follows:

	Regent Road	Nab Top Sanatorium, Marple	Ladywell Sanatorium	Drinkwater Park
Year's total ..	1786·0	2703·0	2294·6	2208·8
Average ..	1683·8	2426·4	2002·8	1953·0

The highest figures were, of course, obtained at Marple, where the atmosphere is much clearer than in Salford.

Attention has previously been directed to the fact that once the potassium iodide solution has become coloured with iodine the speed of the reaction, *i.e.* the amount of iodine liberated slows down rapidly; this can be demonstrated either by adding a known quantity of iodine in a duplicate test, when the amount of iodine liberated on exposure will be less than in the test as ordinarily carried out, or by placing bottles out at short intervals (say 2 hours), when the total amount of iodine liberated will be greater than usual. In order to get further information bearing on, and also possibly to arrive at some quantitative idea of the extent of, this slowing down of the reaction, it was decided to expose a solution of potassium iodide to the light transmitted by various glass filters. For this purpose, eight different types of Chance–Parsons colour filters were used, the potassium iodide solution being held in transparent quartz test-tubes placed behind the filters in such a manner that the only light reaching the tubes was that transmitted by the filters. The effect of a piece of ordinary window glass was also determined. Exposures were made at exactly the same time towards the same portion of the sky, and were of about seven hours' duration, the contents of the tubes being then titrated immediately. The following table gives the average figures for five series of tests:

EFFECT OF CHANCE–PARSONS FILTERS ON POTASSIUM IODIDE TEST

	Blank	Window glass	"Daylight" glass	Blue-green	Ultra-violet	Purple	Light orange	Dark orange	Ruby	Red
Average amount of iodine liberated (5 tests), mg. ..	2·57	2·32	2·26	1·72	0·97	0·73	0·25	0·11	0·07	0·07
Percentage of blank	—	90·3	87·9	66·9	37·7	28·4	9·7	4·3	2·7	2·7

The most striking feature of these results is the fact that the highest figures were obtained when a proportion of both U.V. and visible blue rays were transmitted by the filters, *i.e.* quartz, window-glass, "Daylight" glass and blue-green filter. In the next group come the U.V. and purple filters, both of which transmit a proportion of the U.V. rays, but practically no visible blue rays. Lastly we have the four orange and red filters, which transmit neither U.V. nor visible blue rays, and which all slow down the reaction by at least 90 per cent. In more precise terms, quartz transmits all rays down to about 200$m\mu$ and window-glass down to about 320$m\mu$. The figures supplied by the makers of the filters indicate that the "Daylight" filter transmits down to about 328$m\mu$, the blue-green between 370$m\mu$ and 588$m\mu$, the ultra-violet between 313$m\mu$ and 400$m\mu$ with some transmission above 700$m\mu$, and the purple between 345$m\mu$ and 410$m\mu$ with some transmission above 690$m\mu$. The four orange and red filters do not transmit rays below 500$m\mu$.

There is relatively little difference between the results obtained with quartz, and with quartz and window-glass, suggesting that the shorter U.V. rays do not play a large part in the reaction; on the other hand, the effect of even the light orange filter is very great. Although the experimental accuracy of work with colour filters is somewhat questionable, owing to the difficulty that the various wavelengths overlap, the experiments so far carried out indicate that this reaction is due almost entirely to wavelengths between $300m\mu$ and $500m\mu$.

ASHWORTH'S ULTRA-VIOLET RAY METER.—It has been found that the ordinary photographic paper used in this instrument (*cf.* ANALYST, **1933**, **58**, 690; **1937**, **62**, 667) varies considerably in sensitivity, and therefore potassium dichromate light-sensitive paper was used instead for the observations during the last 10 months of the year.

INTEGRATING SOLARIMETER.—So far as I am aware, only one other instrument of this type is in use in this country, and that is a recording solarimeter at the Meteorological Office, South Kensington. The instrument is essentially a Moll pattern thermopile coupled with a sensitive milliampere-hour-indicator. The solar radiation is therefore transformed into and recorded as, electrical energy, the apparatus having previously been calibrated by exposure to a standard source of radiation. The results are in terms of absolute units of energy and give the total solar radiation, both visible and invisible. The results recorded by the Salford and Kensington instruments (the latter results kindly supplied by the Director of the Meteorological Office) were as follows:

SOLARIMETER—DAILY MEAN RADIATION

(Gramme Calories per Square Centimetre)

Month	Salford	South Kensington
January	11·33	38·5
February	26·55	75·6
March	85·50	160·0
April	122·25	227·0
May	190·50	281·0
June	222·25	377·4
July	177·08	283·0
August	168·75	234·0
September	88·95	185·9
October	48·75	106·0
November	18·00	60·4
December	7·73	30·1

The results show pronounced differences between the two series of observations, especially in the winter months, and they indicate in a striking manner the very considerable screening of daylight by smoke clouds in the air above this City.

G. H. WALKER

Lagos

ANNUAL REPORT ON THE DEPARTMENT OF CHEMISTRY FOR 1938

THE work of the Department of Chemistry (under the direction of Mr. C. L. Southall, B.Sc., A.I.C.) is mainly concerned with the examination of samples and exhibits submitted by various Departments, notably Customs, Medical and Health, and Police. The total number of examinations made during the year was 2615, which was a small increase on the previous year. A large proportion of the work related to water supplies, and involved 912 bacteriological and 172 chemical examinations.

TESTS FOR *B. COLI*.—The authors of the Ministry of Health Bulletin, No. 71, requested water bacteriologists to test Levine's Eosin—Methylene Blue—agar in comparison with the usual MacConkey's neutral red agar, which is not very satisfactory in the tropics. Extensive tests indicated that it was possible when using Levine's agar to distinguish between typical *B. coli* and *B. aerogenes* by direct inspection after incubation for 24 hours at 37° C. The use of this medium has been adopted and is particularly helpful when examinations have to be made on the spot.

PRECIPITIN TEST FOR BLOOD ON WATER-PROOFED MATERIAL.—The precipitin test for blood was applied to 430 exhibits. In one most important case it failed. The prosecution suspected that a rubberised coat had been used to wrap up a recently severed head. There were stains of blood on the fabric, which had been partly washed out, but the precipitin test could not be applied because extracts from unstained portions of the coat all gave positive reactions. Two other raincoats were tested, and, while a heavily rubberised coat gave positive results, another raincoat did not do so. No method of separating the blood from the interfering proofing matter could be discovered, and advice on this point from other workers would be most welcome.

FLUORESCENCE OF SEMINAL STAINS.—There was an increase in the number of exhibits submitted in cases of alleged rape. In this connection it was noticed that some white stains on indigo-dyed woollen cloth showed no fluorescence in ultraviolet light, although perfect spermatozoa were readily extracted from them.

POISONING CASES.—There was a wider range of poisons than in former years and the following substances were isolated from viscera: Strophanthin, hyoscyamine, physostigmine (Calabar bean), thevetin, quinine, sasswood, croton oil, camphor, methyl salicylate, ammonia, caustic alkali, phenol, prontosil, cyanide, mercury and bismuth. In no case was arsenic found, but on several occasions toxic organic material which could not be identified was isolated.

HYDROCYANIC ACID IN LAGOS FOODSTUFFS.—The hydrocyanic acid content of various native foods was estimated colorimetrically by a modification of the method of Childs and Ball (ANALYST, 1935, **60**, 296). Whereas samples of raw material contained as much as 40 p.p.m. of CN, only one sample of prepared foodstuff contained as much as 1 p.p.m. In spite of this, many medical officers are convinced that cyanide poisoning is prevalent, and it is hoped that further samples will be submitted for examination.

COMPOSITION OF HUMAN MILK (AFRICAN).—A sample, taken under conditions that ensured its being genuine and average, contained 5·4 per cent. of fat and 8·8 per cent. of solids-not-fat. Similar abnormal figures have been reported in a few instances from other African Colonies.

NIGERIAN LIGNITE.—A sample was found to have a proximate composition almost identical with that of the brown lignite deposits in Germany.

Hong Kong

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

THE work of the Hong Kong Government Laboratory (under the direction of Mr. C. V. Branson, B.Sc., F.I.C.) differs from that usually associated with a sub-department of this type, in that a considerable amount of work usually done by consulting chemists is done there, the fees being paid into the Treasury. Practically the whole of the official work is chemico-legal.

TOXICOLOGICAL EXAMINATIONS.—The total number of samples examined was 236 as compared with 199 in the previous year; poisons were detected in 164. Suicide again accounted for most of the deaths. Opium, detected in 46 cases, was still the most common agent, but a very large increase in poisons of the lysol type (39) was recorded. Arsenic derivatives were found in 25 cases, barbituric acid derivatives in 8, *Gelsemium elegans* in 8, santonin in 2, mercury in 2, lead in 2, and mydriatic alkaloids in 1.

BOMB OUTRAGES.—The Laboratory was consulted in connection with three bomb outrages. In one of these a parcel was delivered to a house by a private messenger, and, when an attempt was made to open it, it exploded and produced fatal injuries. After investigation of the pieces, it was possible to construct a copy of the bomb; this was produced in Court. The bomb was exploded by means of an electrical contact firing a charge of black powder and broken glass. In the other two cases the bombs were of the Mills type and were filled with a mixture of picric acid, perchlorate and aluminium.

COUNTERFEIT COINING.—There was a great reduction in the number of cases—11 as compared with 78 in 1936. The new nickel coins in circulation are much more difficult to counterfeit than the older coins, so that a further decrease is to be expected.

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT FOR THE YEAR 1938

THE Director (Mr. F. Hirst, M.Sc.) reports that the feeding tests which have been conducted at the Rowett Institute, Aberdeen, over a period of two years (*cf.* ANALYST, 1938, **63**, 823) are now completed. The results, to be published shortly, do not show any definite difference in breeding data, lactation, growth and other factors between rats bred and fed on a diet consisting entirely of canned foods and those on a similar diet of the corresponding foods cooked in the ordinary way. They confirm the results obtained in France and the United States of America, and, when taken in conjunction with those of other workers on the vitamin and mineral salt content, indicate that the nutritional value of canned products compares favourably with that of home-cooked food.

The study of the distribution and losses of the various mineral constituents of certain vegetables during home cooking and canning, which was begun about the same time as the feeding experiments at Aberdeen, has also been completed, and the results are described in a section of this report. These and other health aspects of canned foods are being reviewed in collaboration with a member of the staff of the Rowett Research Institute, and it is hoped that a comprehensive bulletin on the subject will be ready for publication in the near future.

During the year under review 719 technical enquiries were answered by post and probably a greater number by telephone. In addition, 326 samples of canned products were examined and reported on, and 104 canner's thermometers and pressure gauges were tested. The subjects investigated at the Station included the following:

FRUIT-GUM IN PLUMS.—In the previous Report (*cf.* ANALYST, 1938, **63**, 823) it was suggested that the site at which surface spots of gum developed might be correlated with the presence or absence of internal gum. In the season under review it was noted that soft spots of gum developed very extensively on the distal ends of Victoria plums grown locally. Many of these spots hardened and fell off as the fruit ripened. Thirty-six of such plums were canned, and in thirty of them severe internal gumming was noted in the canned product.

DRAINED WEIGHT OF ENGLISH CANNED FRUIT.—The results of an investigation by the Director and W. B. Adam, in which the figures obtained during the past ten years were studied, indicated that the degree of ripeness, the strength of the syrup used, and the conditions of processing all have some influence on the drained weight; this also alters during storage. The wide difference between the average and minimum drained weights recorded makes it difficult to establish standards based on drained weights. The texture of the canned fruit is of such importance in this connection that some reference to wholeness or firmness of the fruit would appear to be essential in framing appropriate regulations. Such regulations could better be based on the average drained weight of a definite number of cans of each commercial brand than on a minimum figure which applied to every can packed.

COMPOSITION AND CANNING PROPERTIES OF LOGANBERRIES AND BLACKBERRIES.—The primary object of this work by the Director was to compare two pairs of closely allied fruits—the *Loganberry* and the *Phenomenal Berry*, and *Black Diamond* and *Himalayan Giant* blackberries. The following table shows the chief characteristics of the two types of fruit canned in 1936, 1937 and 1938. The figures (except for 1938) are an average of all the results obtained. Acidity is expressed as anhydrous citric acid:

LOGANBERRIES AND PHENOMENAL BERRIES

	Composition of fresh fruit			Canned fruit	
	Acidity Per Cent.	Soluble solids Per Cent.	Insol. solids Per Cent.	*p*H	Loss in weight Per Cent.
1936					
Loganberries ..	2·80	8·8	5·6	2·85	14·5
Phenomenal Berries	2·85	8·8	5·7	2·82	15·1
1937					
Loganberries ..	2·56	9·5	5·8	2·96	12·3
Phenomenal Berries	2·56	10·1	5·6	2·88	12·1
1938					
Loganberries ..	2·74	11·0	5·1	2·76	15·3
Phenomenal Berries	2·72	10·9	4·9	2·77	17·9

BLACKBERRY VARIETIES

	Composition of fresh fruit			Canned fruit	
	Acidity Per Cent.	Soluble solids Per Cent.	Insol. solids Per Cent.	*p*H	Loss in weight Per Cent.
1936					
Black Diamond ..	2·00	9·0	4·6	3·03	10·1
Himalayan Giant ..	2·03	8·7	4·0	3·01	9·7
1937					
Black Diamond ..	2·54	10·6	6·5	2·90	12·3
Himalayan Giant ..	2·53	10·3	7·4	2·92	12·1
1938					
Black Diamond ..	1·74	9·7	5·6	2·95	19·7
Himalayan Giant ..	2·00	9·0	5·6	2·93	17·3

Very little difference was noted in the chemical composition of the *Loganberry* and *Phenomenal Berry*. In canning, the latter could be distinguished by its paler colour. The acidity and *p*H of loganberries does not alter appreciably throughout the season, but the total sugar-content appears to increase. No difference in chemical composition or canning properties of the two varieties of blackberries could be detected. Ripening changes in cultivated blackberries are considerable; in particular, the *p*H changed from 2·7 to 3·4 during the ripening of the fruit in the edible state.

MINERAL-CONTENT OF CANNED VEGETABLES.—In this investigation (by G. Horner) the results indicate that the losses of mineral constituents in the canning of vegetables are of approximately the same magnitude as those that occur in cooking in the home. Calcium is the only element that normally shows an increase, the calcium present in the water being readily absorbed by vegetables during the blanching process; the increase is roughly proportional to the hardness of the water. Calcium is not evenly distributed between the solid and liquid portions of the contents of the can, the ratio of the percentage of calcium in the solids to that in the liquid ranging from 1·35 with fresh peas to 2·11 with carrots. A loss of magnesium is recorded in all the operations. The variations shown are partly due to changes in weight, but the amount of calcium present and the common salt in the cooking and canning liquids also have some effect on the behaviour of magnesium. Potassium salts are freely soluble, and their concentrations in the solid and liquid portions are virtually equal. A blanch of only three minutes in boiling water produces losses of 30 to 40 per cent., and the total losses on cooking and canning may be as high as 60 to 70 per cent. This suggests that the potassium salts in vegetables are distributed near the surface rather than in the interior. A loss of phosphorus occurs in all the operations; for example, with fresh peas, 12 per cent. in blanching, 41 per cent. in canning and 35 per cent. in home cooking. The concentration of phosphorus in the solid portion of canned vegetables is usually about double that in the liquid, indicating that roughly about half of the phosphorus is in a soluble form. Chlorine constituents of vegetables are freely soluble and become evenly distributed throughout the contents of the can.

THERMOPHILIC BACTERIA IN SUGAR.—It has been conclusively shown that sugar may be the direct cause of the entry of such large numbers of thermophilic bacteria into the cans that sterility is not attained and spoilage may ensue. When such sugar is used, scrupulous attention to cleanliness of the plant cannot eliminate the risk. In the present investigation (by T. G. Gillespy) previous work on the subject is reviewed and the results of experiments are described. It was found that many samples of sugar refined in Britain were unsuitable for canning. When unsuitable sugars were used in canning experiments with peas, sterility was not attained by normal processing. Bacteriological analyses of samples taken during sugar refining show the number of aerobes and anaerobes present at various stages. It is probable that there will be an increasing demand for guaranteed canners' sugar in this country.

COMPOSITION AND TEXTURE OF DRIED PEAS.—This investigation has been continued by W. B. Adam (*cf.* ANALYST, 1937, **62**, 738; 1938, **63**, 823). It was found that there was little difference in the texture of peas grown from seed planted at periods from March to May. Artificial drying of shelled mature peas for six to seven hours at 120° F. and 160° F. appeared to toughen the texture very slightly.

The following wide variations were noted in the percentages of the various mineral constituents in the ash: CaO, 1·8 to 5·0; MgO, 5·2 to 8·3; K_2O, 34 to 39; P_2O_5, 22 to 42. The effect of varying the temperature and time of ashing was studied. The sample of peas used was stored under conditions of uniform temperature and humidity, and in each test 20 g. were weighed into silica dishes and ignited in a muffle-furnace until the last traces of carbon had disappeared. The temperatures given in the following table are only approximate and were determined by means of thermo-couples and also by fusion of various pure salts placed near the silica dishes.

Conditions of ashing		Composition of ash				
Temp. °C.	Time Hours	Ash Per Cent.	CaO Per Cent.	MgO Per Cent.	P_2O_5 Per Cent.	K_2O Per Cent.
500	24	2·86	2·34	5·66	39·8	43·6
630	18	2·83	2·52	5·69	40·0	42·9
750	8	2·78	2·44	5·94	40·6	42·3
900	2	2·68	2·60	6·15	40·3	41·6

In another set of tests peas were ashed for various times at each of the four temperatures used before and the following results were obtained:

Conditions of ashing		
Temp. °C.	Time Hours	Ash Per Cent.
500	24	2·86
	36	2·80
	38	2·80
630	18	2·96
	27	2·87
	36	2·84
750	8	2·76
	12	2·74
	16	2·74
900	2	2·78
	3	2·71
	4	2·66

These data indicate that the greatest risk of variable results appears to be due to incomplete ashing rather than to excessive heating, although ashing at a high temperature resulted in a slight loss of potassium. Ashing in powdered form was found to be less satisfactory than ashing the whole peas.

STUDIES ON THE MOULD *BYSSOCHLAMYS FULVA*.—In continuation of his investigation (*cf.* ANALYST, 1938, **63**, 824), T. G. Gillespy has confirmed the finding that the asci of *B. fulva* are most resistant to heat at *p*H 5. The protective effect of sucrose in solutions has been clearly shown; nearly 10 per cent. of the asci survived for 12 minutes at 90° C. when heated in fruit syrups. Ascospores were found to be susceptible to intermittent heating. The optimum conditions for the shortest intermediate heating period were as follows:—Suspending medium *p*H 3 (or lower); initial and final heatings, 10 minutes at 77° C.; intermediate temperature, 46° C. All ascospores were destroyed when the intermediate period was 30 minutes. When heated at 77° C., without a break, 38 per cent. survived.

Metropolitan Water Board

THIRTY-SECOND ANNUAL REPORT ON THE RESULTS OF THE CHEMICAL AND BACTERIOLOGICAL EXAMINATION OF THE LONDON WATERS FOR THE TWELVE MONTHS ENDED 31ST DECEMBER, 1937*

OWING to the unfortunate illness of Colonel Harold early in May last year and its tragic termination in July, the completion of his report by the Deputy Director of Water Examinations, Mr. Denison B. Byles, was delayed. Tribute is paid in the preface by his deputy to Colonel Harold and to his outstanding work for the Board during his four years' service.

The Report consists of an introduction and seventeen sections under the following headings: (1) Bacteriological Section; (2) Biological Section; (3) Chemical Section; (4) Works Efficiency; (5) Walton Works; (6) Kempton Park Works; (7) Stoke Newington Works; (8) Wells; (9) Prefiltration Waters; (10) Resistance to Filtration and Microscopical appearances of Prefiltration Waters; (11) Epping Sewage and Cobbin's Brook; (12) Waltham Abbey Well; (13) Complaints; (14) The

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* By Lt.-Col. C. H. H. Harold, O.B.E., M.D., Ch.B., D.P.H. 1939. Published by P. S. King & Son, Ltd., 14, Great Smith Street, Westminster. Price 10s. 6d.

Thames as a source of Potable Water; (15) Meteorological Notes; (16) Routine Tables; (17) The Flow and Bacteriology of Underground Water in the Lee Valley.

This Report, in common with previous Reports of Colonel Harold and his predecessor, contains matter of very considerable interest to all who are engaged in water examinations and undertakings, as well as particulars about the London supply. A brief account of the main points of general interest only is given in this summary.

SECTION I: THE BACTERIOLOGICAL SECTION

COMPARISON OF THE EFFICIENCY OF ENRICHMENT MEDIA FOR THE PRIMARY ISOLATION OF COLIFORM BACILLI.—The enrichment media tested were: MacConkey's broth, Brilliant Green Bile broth and Dominick–Lauter's Methylene blue-bromcresol-purple broth. These were tested on 7277 samples, and it was found that the results obtained were, on the whole, very similar with all three. Brilliant Green Bile broth yielded 786 positives of which 585 were typicals, MacConkey broth yielded 762 positives with 563 typicals, and Dominick–Lauter broth 744 positives with 543 typicals. MacConkey's broth is judged to be in no way inferior to the other two and superior to them for stored waters.

THE INDOLE PRESUMPTIVE TEST.—This test, which is applied to filtered waters, consists of cultivation in MacConkey's broth and in peptone water for 18 to 24 hours; samples showing gas in the former and indole in the latter are reported at once to the engineers as unsatisfactory. A certain number of indole productions, however, are not due to *B. coli*, thus unduly weighting the number of reported samples and leading to the inference that more *B. coli* are present than there actually are.

It was decided to substitute a tube of Brilliant Green Bile broth for peptone water, and to observe the production of gas instead of indole. The value of being able to report unsatisfactory filtration so promptly—within 18 to 24 hours—that a filter can be put out of commission immediately is obvious.

USEFUL MODIFICATION OF KOSER'S CITRATE MEDIUM.—Growth in this medium, indicated by turbidity, is one of the tests to distinguish *intermediate aerogenes-cloacae* types from *B. coli type I*. As an aid to the reading of turbidity it was found that addition of bromothymol blue and adjustment to *p*H 6·4 to 6·6 gave a colour-change from apple-green to blue-green or deep blue with citrate-positive cultures, some of the citrate being converted into bicarbonate and carbonate. This useful device might well be adopted in other laboratories.

APPLICATION OF THE MACCONKEY AND KOSER'S CITRATE TESTS TO THE QUANTITATIVE ESTIMATION OF *COLI* AND *AEROGENES* ORGANISMS IN RAW WATER.—A comparison is made of three methods: (1) The customary routine method of the Board. (2) Method (*a*) [modification* of Method III of Wilson†]. Two sets of MacConkey's broth cultures are prepared, and one is incubated at 42° C., and the other at 44° C. for 24 hours. Tubes showing acid and gas at 42° C. are subcultured into citrate broth and incubated at 37° C. for 48 hours. Acid and gas at 44° C. indicate *B. coli type I*, and turbidity in citrate broth at 37° C. indicates intermediate-aerogenes-cloacae types. (3) Method (*b*) [modification* of Method IV of Wilson]—one set of MacConkey's broth cultures is incubated at 42° C. and, after 24 hours, all positives are subcultivated into MacConkey's broth and incubated at 44° C., and into citrate broth and incubated at 37° C. The rationale is the same as for method (*a*), except that delicate organisms that might, and do, fail to grow at 44° C. grow after preliminary cultivation at 42° C., and that the same inoculum of water is used, and *B. coli type I* and intermediate-aerogenes organisms are thus given an equal chance.

* The modification consists only in incubating at 42° C. instead of 37° C.

† Vide *The Bacteriological Grading of Milk.*

The enumeration of Coliform bacilli by methods (*a*) and (*b*) was checked by subsequent plating out, isolation and identification of types. Method (*a*) was found to inhibit the growth of many typicals; method (*b*) did so only in one instance. The latter method was therefore selected for further trials with 56 samples of raw water. It was found that by method (*b*), which merely involves presumptive selective media and temperatures and takes only 72 hours, 46 out of 56 samples were correctly analysed as regards their *Coli-aerogenes* contents, 96 hours being required by the routine tests. While, therefore, it is not as good as the routine test, in view of its far greater simplicity it should be of considerable value where laboratory facilities are limited, and where time is an important consideration.

SECTION II.—THE BIOLOGICAL SECTION

The outstanding investigations under this heading were: (1) the study of algal flora in standing storage reservoirs and the conditions which lead to a fall in the nitrate nitrogen content and the development of blue-green algae, such as *Oscillatoria*, and (2) the increase in volume of sand grains in primary filters by deposition of calcium carbonate, leading to less efficient filtration. It is shown that the deposition of calcium carbonate is not due to removal of carbon dioxide and consequent alteration of the carbonate-bicarbonate equilibrium, and that it is more probably due to biological agencies. Certain suggestions are made as to possible remedial measures.

SECTION XVI.—ROUTINE TABLES

These show absence of typical *B. coli* in 100 ml., in 99·6 per cent. of all samples of Thames-derived waters examined (3163); in 99·0 per cent. of all London waters as supplied to consumers (7168 samples); in 98·4 per cent. of all samples from the Kent wells; in 96·9 per cent. of samples from Lee Valley wells—a very high standard of purity.

SECTION XVII.—THE FLOW AND BACTERIOLOGY OF UNDERGROUND WATER IN THE LEE VALLEY

Previous tests with fluorescein proved that there is direct fissure communication between the swallow holes at North Mimms and South Mimms and Chadwell Spring, Amwell Marsh Well and Hoddeston Well, and that water travels from these swallow holes to the spring and wells—a distance of some 10 miles—in 3 days. Such a rate provides little possibility of purification. Bacteriological examinations were made of the impure water flowing into the swallow holes and of the water from the spring and wells, and the frequence and distribution of the *Coli-aerogenes* types present at the sampling points was worked out. Generally speaking, it was found that reduction of pollution of the water from the Lee Valley was two hundredfold in drought, but in flood times only tenfold. The relative numbers of *Coli-aerogenes* bacteria were determined by direct plating, so that the original proportions should not be modified by preliminary cultivation in enrichment media.

It was found that from all sampling points *B. coli type I* accounted for 74 per cent. *intermediate type I* for 9·6 per cent., *B. coli type II* for 5·4 per cent., *aerogenes-cloacae types* for 4·1 per cent., *intermediate type II* for 3·8 per cent., and *irregular strains* for 3·0 per cent., and that with minor differences these proportions held whether the samples were from the swallow holes or from the spring and wells. It is concluded that when assessing the purity of samples in this country, the intermediate and aerogenes types, representing some 25 per cent., cannot be ignored. It is probable, however, though the report gives no data on this point, that the number of samples of this contaminated water failing to show the presence of *B. coli type I* in one or other of the quantities, taken in ordinary routine and with the use of enrichment media examination, would be quite small. D. R. WOOD

British Pharmacopoeia Commission

REPORTS OF COMMITTEES ON PHARMACEUTICAL CHEMISTRY*

WE are asked to state that these Reports include recommendations relating to the monographs of the British Pharmacopoeia, 1932, as amended by the Addendum, 1936. They also include draft monographs on new substances which the Commission have provisionally accepted for inclusion in the next Pharmacopoeia. In accordance with former practice these Reports are made public, in order to provide an opportunity for medical practitioners, pharmacists, analysts, manufacturers and others who may be interested, to criticise them and to suggest emendations before the preparation of the new Pharmacopoeia reaches its final stage.

REPORT No. 11

I. REPORT OF THE SUB-COMMITTEE ON ESSENTIAL OILS.—The Sub-Committee (Messrs. T. Tickle, *Chairman*, C. T. Bennett, S. W. Bradley, T. T. Cocking, C. E. Sage, and W. H. Simmons) recommend that the following monographs and appendixes of the B.P. 1932, as amended by the Addendum, 1936, should be continued without change:—Oleum Abietis, Oleum Anethi, Oleum Anisi, Oleum Cajuputi, Oleum Cari, Oleum Eucalypti, Oleum Lavandulae, Oleum Menthae Piperitae, Oleum Santali Australiensis.

Appendix XI. B. The Determination of Free Alcohols in Volatile Oils.
Appendix XI. C. The Determination of Aldehydes in Volatile Oils.
Appendix XI. D. The Determination of Carvone in Oil of Caraway, and in Oil of Dill.
Appendix XI. E. The Determination of Cineole in Oil of Cajuput and in Oil of Eucalyptus.

Changes or additional requirements are recommended in connection with: Eucalyptol, Oleum Cadinum, Oleum Caryophylli, Oleum Chenopodii, Oleum Cinnamomi, Oleum Coriandri, Oleum Limonis, Oleum Myristicae, Oleum Rosmarini, Oleum Santali, Oleum Terebinthinae.

Appendix XI. A. (Determination of the Esters in Volatile Oils.) Changes are proposed to bring the method into agreement with the Society of Public Analysts' method.

Appendix XI. E. (Determination of Cineole.) The present Appendix should be retained, with the omission of the reference to Eucalyptol and the addition of the direction that the *o*-cresol is to be accurately weighed.

The following new monographs are proposed:—Oleum Amygdalae Volatile Purificatum, Oleum Camphorae Rectificatum, Appendix XI. C. [3] (Purified Volatile Oil of Bitter Almond), Determination of Volatile Oil in Crude Drugs (a modification of the apparatus and method of Cocking and Middleton is recommended and described).

II. REPORT OF THE SUB-COMMITTEE ON FIXED OILS, FATS, WAXES, RESINS AND SOAPS.—The Sub-Committee (Messrs. T. Tickle, *Chairman*, E. R. Bolton,† N. Evers, J. R. Nicholls, and W. H. Simmons) recommended that the following monographs of the B.P. 1932, as amended by the Addendum, 1936, should be continued without change:

Cera Alba, Cera Flava, Oleum Amygdalae, Oleum Hydnocarpi, Oleum Hydnocarpi Aethylicum, Paraffinum Molle Album, Paraffinum Molle Flavum, Sevum, Appendix IX. A. (Test for Absence of Cottonseed Oil in Other Oils), Appendix IX. B. (Test for the Absence of Sesame Oil in Other Oils), Appendix X. B. (Determination of the Saponification Value of Fixed Oils and Fats).

It is recommended that changes or additional requirements should be inserted for:

Oleum Arachis, Oleum Gossypii Seminis, Oleum Lini, Oleum Olivae (Fitelson's colour test for Tea-seed Oil recommended), Oleum Ricini, Oleum Sesami, Oleum Theobromatis, Paraffinum Durum, Paraffinum Liquidum, Sapo Animalis (tests redrafted in accordance with new methods published by the Society of Public Analysts), Sapo Durus (new S.P.A. methods), Sapo Mollis (new S.P.A. methods), Appendix IX. C.—Test for Absence of Arachis Oil in Other Oils (new directions proposed), Appendix X. A.—Determination of the Acid Value of Fixed Oils, Fats and Resins, Appendix X. C.—Determination of Iodine Value of Fixed Oils and Fats (Pyridine bromide method recommended), Appendix X. D.—Determination of Unsaponifiable Matter in Fixed Oils and Fats (S.P.A. method recommended), Oleum Hippoglossi. (It is recommended *inter alia* that when a statement is made of the number of units of vitamin D in Halibut Liver Oil, the units enumerated should be the units described under the biological assay of antirachitic vitamin [vitamin D].)

III. REPORT OF THE SUB-COMMITTEE ON THE ASSAY OF GALENICALS.—The Sub-Committee (Messrs. T. Tickle, *Chairman*, T. T. Cocking, C. E. Corfield, J. Evans, N. Evers, D. C. Garratt,

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* Reports Nos. 11 and 12. May, 1939. Published by Authority of the General Medical Council, 44, Hallam Street, London, W.1. Price 1s. 6d. each.

† Deceased February, 1939.

W. H. Linnell, J. R. Nicholls and A. D. Powell) recommend that the following assays should be continued without change:

Extractum Filicis, Linimentum Camphorae, Liquor Ammonii Acetatis Dilutus, Liquor Ammonii Acetatis Fortis, Liquor Arsenicalis, Liquor Arseni et Hydrargyri Iodidi, Liquor Calcii Hydroxidi, Liquor Formaldehydi, Liquor Glycerylis Trinitratis, Liquor Iodi Fortis, Liquor Iodi Mitis, Liquor Iodi Simplex, Liquor Magnesii Bicarbonatis, Liquor Potassii Hydroxidi, Liquor Quininae Ammoniatus, Liquor Sodii Chloridi Chirurgicalis, Oxymel, Phenol Liquefactum, Pilula Hydrargyri, Spiritus Aetheris Nitrosi, Syrupus Ferri Iodidi, Unguentum Hydrargyri Dilutum, Unguentum Hydrargyri Compositum, Appendix XII. A. (Determination of Ash), Appendix XII. B. (Determination of Acid-insoluble Ash), Appendix XII. C. (Determination of Water-soluble Ash), Appendix XII. D. (Determination of Alcohol-soluble Extractive), Appendix XII. E. (Determination of Water-soluble Extractive), Appendix XII. G. (Determination of Industrial Methylated Spirit).

It is recommended that changes or additional requirements be inserted for the following:

Extractum Malti (limit test of diastatic value corresponding approximately to 15° Lintner), Extractum Malti cum Oleo Morrhuae, Ferri Carbonas Saccharatus, Glycerinum Acidi Borici, Glycerinum Acidi Tannici, Glycerinum Boracis, Glycerinum Phenolis, Jalapa, Linimentum Belladonnae, Linimentum Saponis, Linimentum Camphorae, Linimentum Camphorae Ammoniatum, Linimentum Terebinthinae, Linimentum Terebinthinae Aceticum, Liquor Cresolis Saponatus, Liquor Ferri Perchloridi (lead limit of 15 p.p.m. proposed), Liquor Hydrargyri Perchloridi, Liquor Plumbi Subacetatis Fortis, Oxymel Scillae, Pilula Ferri Carbonatis, Spiritus Ammoniae Aromaticus, Spiritus Camphorae, Syrupus Ferri Phosphatis Compositus, Tabella Glycerylis Trinitratis (assay methods still under investigation), Unguentum Acidi Borici, Unguentum Acidi Salicylici, Unguentum Acidi Tannici (no suitable method yet available), Unguentum Hydrargyri Ammoniati, Unguentum Hydrargyri Oleati, Unguentum Hydrargyri Subchloridi, Unguentum Phenolis, Unguentum Sulphuris, Unguentum Zinci Oleatis, Unguentum Zinci Oxidi.

In Appendix XII. F.—Determination of Alcohol Content—Method II has been revised. In the *Alcohol Limits Table* the following changes should be made.

	Methods of determining alcohol content	Alcohol limits per cent. v/v of ethyl alcohol
Extractum Ipecacuanhae Liquidum ..	III	75–80
Infusum Aurantii Concentratum	III	21–25
Infusum Buchu Concentratum	III	21–25
Infusum Caryophylli Concentratum ..	III	22–25
Spiritus Aetheris Nitrosi	II	84–87
Tinctura Capsici	III	57–60
Tinctura Catechu	I	37–40
Tinctura Cinchonae	I	63–66
Tinctura Ipecacuanhae	III	20–24
Tinctura Opii Camphorata	II	56–60
Tinctura Rhei Composita	III	48–53
Tinctura Senegae	I*	55–58
Tinctura Zingiberis Fortis	III	80–88

REPORT No. 12

I. Report of the Sub-Committee on Synthetic Chemicals.—The Sub-Committee (Dr. W. H. Linnell, *Chairman*, Messrs. J. W. Blagden, F. H. Carr, A. J. Ewins, H. King, A. D. Powell, and S. Smith) recommend that changes or additional requirements be inserted for:

Acriflavina, Adrenalina, Barbitonum, Barbitonum Solubile, Calcii Gluconas, Carbromalum, Chloralis Hydras, Cinchophenum, Dextrosum, Fluoresceinum Solubile, Indicarminum, Iodophthaleinum, Lactosum, Methylthioninae Chloridum, Phenobarbitonum, Phenobarbitonum Solubile, Salicinum, Thymol.

New Monographs.—Acidum Mandelicum (Phenylglycollic Acid), Calcii Laevulas, Calcii Mandelas, Cyclopropanum, Liquor Nucleotidi, β-Phenylisopropylamine, β-Phenylisopropylamine Sulphate, Pyridine-β-Carboxylic Acid Diethylamide, Sulphanilamidum, Theophyllina cum Aethylenediamine, Urethanum.

II. Report of the Sub-Committee on Alkaloidal Assays.—The Sub-Committee (Dr. W. H. Linnell, *Chairman*, Messrs. N. L. Allport, C. E. Corfield, N. Evers, D. C. Garratt, A. D. Powell, and L. W. Ragg) recommend that changes or additions should be made for the following:

Aconitum, Extractum Ipecacuanhae Liquidum, Ipecacuanha Pulverata, Liquor Morphinae Hydrochloridi, Liquor Strychninae Hydrochloridi, Lobelia (Society of Public Analysts' method),

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* Acidify with *dilute sulphuric acid* before the first distillation.

Opium, Pulvis Ipecacuanhae et Opii, Syrupus Ferri Phosphatis cum Quinina et Strychnina, Tinctura Opii Camphorata, Theobromina et Sodii Salicylas, Theophyllina et Sodii Acetas (under investigation).

Alkaloidal Salts.—The Sub-Committee have agreed to accept as a general principle that for any alkaloidal salt, the purity of which can be accurately controlled by physical measurements and by chemical tests for purity, a chemical assay is unnecessary. It is recommended that no assay should be prescribed for: Apomorphinae Hydrochloridum, Atropinae Sulphas, Cocainae Hydrochloridum, Ephedrinae Hydrochloridum, Ergotoxinae Aethanosulphonas, Hyoscinae Hydrobromidum, Physostigminae Salicylas, Pilocarpinae Nitras. Changes in the assay of a number of alkaloidal salts are recommended, and a new monograph for Morphinae Sulphas is proposed.

British Standards Institution

THE following Standard Specifications have been issued:*

NO. 844—1939. BRITISH STANDARD METHODS FOR THE TESTING OF VEGETABLE ADHESIVES.

These methods are intended to apply to such vegetable adhesives as are manufactured from starch or from material containing a high proportion of starch, *e.g.* wheat flour and potato starch. Typical adhesives are crystal gums, dextrins and water-soluble pastes and powders.

The physical and chemical properties of vegetable adhesives depend, first, on the nature of the raw materials, and secondly, on the methods of processing. It is not possible to draw up any simple test that will evaluate completely the quality of an adhesive, or its suitability for a particular trade. The tests included, however, provide indications of the behaviour of the adhesive in use, and may be taken as reliable criteria of the quality of different deliveries.

The tests described comprise methods for determining moisture-content, acidity, alkalinity and *p*H value, ash, chemical residues, colour, efficiency of adhesion, foam, keeping quality and viscosity. Some of the physical tests are of an empirical nature (*e.g.* the foam test), but if the Methods are closely followed, they will give consistent results which will afford useful information both to the manufacturer and to the user. Some work has been done on Tackiness, Rate of Setting, and Viscosity at machine consistencies, but the tests have not yet been sufficiently developed to admit of standardisation.

Where possible, the tests are divided into two classes: A.—*Approximate Tests*, which have been found satisfactory for routine testing. B.—*Standard Tests*, which, in the hands of skilled workers, give more precise and reliable results than the approximate tests.

The following directions, *inter alia*, are given for the tests:

Moisture-content is defined as the percentage loss in weight of the sample as received, when the adhesive is dried at 105°–110° C. to constant weight. Liquids and pastes are first mixed with recently ignited silver sand.

Alkalinity, Acidity and pH.—Fifty ml. of a solution containing 10 g. of adhesive in 250 ml. of water are titrated with 0·1 *N* hydrochloric acid, with phenolphthalein as indicator. The alkalinity is calculated as the percentage of sodium hydroxide on the moisture-free weight. If acid, the sample is titrated with 0·1 *N* sodium hydroxide solution, with methyl orange as indicator, and the acidity is expressed as the percentage of hydrochloric acid on the moisture-free weight.

To determine the *p*H value 5 g. of the sample are dispersed in 100 ml. of freshly-boiled distilled water, and the *p*H is determined by a standard electrometric method. A complete titration curve is prepared by plotting the *p*H values, obtained after successive small known additions of 0·1 *N* hydrochloric acid (or 0·1 *N* sodium hydroxide solution), against the amounts of acid or alkali added.

Ash.—Five g. are incinerated in a platinum basin over a low flame at a dull red heat (not exceeding 500°–550° C.).

Chlorides.—The ash is extracted with hot distilled water and filtered, and the filtrate is neutralised with acetic acid (or ammonia), treated with 0·1 ml. of 10 per cent. acetic acid, and titrated with standard silver nitrate solution (1 ml. ≡ 0·01 g. of sodium chloride), 1 ml. of 10 per cent. potassium chromate solution being used as indicator. To avoid the possibility of loss of chlorides by volatilisation, the adhesive (in solution) may be dried and ignited with an equal weight of chloride-free lime, the residue extracted with boiling water, and the chloride determined in the filtrate.

Reducible Sulphur.—The adhesive is treated in a special flask (described and illustrated) with 10 ml. of pure sulphur-free phosphoric acid and 1 g. of pure (not activated) zinc, the flask is heated on a steam-bath for one hour, so that the gases evolved pass through filter-paper impregnated with a 10 per cent. w/v solution of lead acetate, and the sulphide stain is compared with standard stains produced in a similar manner.

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* Obtainable from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 2d. each.

Colour.—The colour of the adhesive is compared with that of an agreed standard adhesive, the samples being spread in thin films of equal thickness on glass and allowed to dry at a temperature not higher than 50° C. If there is no agreed standard adhesive, the colour shall be compared with agreed standard coloured strips. In cases of dispute the colour shall be measured by a standard photometric method.

Efficiency of Adhesion.—A uniform film of the adhesive is applied by means of a brush to a strip (1 inch wide) of one of the materials, and immediately afterwards a similar strip of the second material is applied to the glued place and firmly pressed down by hand. The strips are left for the times specified in the following table, after which the joint strength is assessed by attempting to separate the two strips by peeling. If they can be separated only by continuous disruption of the surfaces (however slowly the peeling is carried out), the efficiency of adhesion is considered satisfactory. In the Standard Test the materials are kept flat until dry by placing them (under specified conditions) under a load of 1 kg., and standard conditions of humidity (34 and 66 per cent.) are maintained.

Class of material	Drying time	Time under specified load
Paper and cardboard	Not less than 6 hours	½ hour
Transparent cellulose material	„ „ „ 1 week	24 hours
Paper and cardboard with a finish or lining of wax, varnish lacquer or metallic foil ..	„ „ „ 1 „	24 „

Maintaining Standard Humidity.—A humidity of 34 per cent. is obtained over magnesium chloride crystals at temperatures between 18° and 24° C., and 66 per cent. humidity is obtained over a saturated solution of sodium nitrite at temperatures between 18° and 24° C.

Foam.—Five g. of the adhesive are dispersed in 50 ml. of water, and the mixture is left for 30 minutes in a graduated stoppered 100-ml. cylinder (B.S. 604) at 25° C. ± 0·2° C. The cylinder is then shaken vigorously with a throw of about 12 in., at a rate of three shakes per second, for one minute, after which the time required for the height of the liquor to correspond to 45 ml., and also the volume of the foam above the liquid, are recorded.

Keeping Quality.—Five g. of adhesive are dispersed in 20 ml. of sterile distilled water and transferred to a Petri dish (B.S. 611), which is covered and incubated at 40° C. Every 24 hours the Petri dish is removed from the incubator and allowed to cool before inspection, and the periods when putrefaction or moulds (or both) occur are noted.

Viscosity.—Owing to the lack of a suitable method for such viscous materials, the method provisionally recommended is the determination of the dilution necessary to obtain a definite viscosity. The dilution of a dispersion of 100 g. of adhesive in distilled water at 20° C. shall be such that the viscosity is 500 centistokes (CS), when determined by the method described in Clause 5 of B.S. 188.

NO. 849—1939. BRITISH STANDARD SPECIFICATION FOR BURETTES AND BULB BURETTES.

BURETTES.—The series includes the following sizes:

Total capacity 1 ml. sub-divided into 0·01 ml. intervals.
„ „ 2 „ „ „ „ 0·02 „ „
„ „ 5 „ „ „ „ 0·02 „ „

„ „ 5 „ „ „ „ 0·05 „ „
„ „ 10 „ „ „ „ 0·02 „ „
„ „ 10 „ „ „ „ 0·05 „ „

„ „ 10 „ „ „ „ 0·1 „ „
„ „ 25 „ „ „ „ 0·05 „ „
„ „ 25 „ „ „ „ 0·1 „ „

„ „ 50 „ „ „ „ 0·1 „ „
„ „ 100 „ „ „ „ 0·2 „ „

BULB BURETTES.—The series includes the following sizes:

Total capacity ml.	Bulb capacity ml.	Range and sub-division of scale ml.
45	20	20 to 45 in 0·05 ml. intervals
65	40	40 „ 65 „ 0·05 „ „
85	60	60 „ 85 „ 0·05 „ „
105	80	80 „ 105 „ 0·05 „ „

For each series definitions of capacity and tolerances on capacity are given, and there are specifications for the material, dimensions, finish of top, stopcocks, jet, delivery time, graduation marks and (for the bulb burettes) shape of bulb.

DRAFT REVISED BRITISH STANDARD NO. 410, FOR TEST SIEVES.

A limited number of copies of this Draft Specification are available for purposes of technical comment. Applications for copies, and comments thereon, should be addressed to the British Standards Institution.

BRITISH STANDARDS FOR A.R.P. REQUIREMENTS

The Home Office Air Raid Precautions Department has arranged with the British Standards Institution to prepare and issue on their behalf a special A.R.P. series of British Standards for Air Raid Precaution purposes.

The preparation of these Standards will be under the control of a special Advisory Committee and, in accordance with the usual practice of the B.S.I., will be carried out in the closest co-operation with Government Departments and the industry concerned.

All communications relating to this work should be addressed to the British Standards Institution, 28, Victoria Street, Westminster, S.W.1.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Alcohols as a Measure of Spoilage in Canned Fish. D. A. Holaday. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 418–420.)—During a study of spoilage in canned fish it appeared that a determination of the amount of alcohols present would afford a reliable index of decomposition. The method used for the determination of alcohols was essentially that of Friedmann and Klaas (*J. Biol. Chem.*, 1936, **115**, 47), depending upon controlled oxidation by alkaline potassium permanganate solution following the removal of interfering substances, and which is specific for the alcohols as a group. Since more than one alcohol may participate in the reaction, the results are expressed as ml. of 0·02 *N* potassium permanganate solution per 100 g. of sample. Fresh samples contain a small amount of alcohols, and this amount increases progressively as decomposition proceeds. The results found with 3 samples ranging in quality from fresh to decomposed were as follows: mackerel, 3·2 to 4·2, 8·6 to 18·0, 27·6 to 70·0; salmon, 3·7 to 7·1, 6·5 to 17·2, 25·2 to 62·2; sardines, 3·3 to 10·2, 11·6 to 27·3, 65·8 to 117·6. To identify the alcohols present the distillate (2·6 litres) from 360 g. of putrid fish was purified as described (*loc. cit.*) and concentrated by a system of fractional distillation to a volume of 8 ml. From 2 ml. of this distillate fractionation in a micro-apparatus yielded a concentrate of 0·05 ml. This had a strong odour of ethyl alcohol, and the m.p. of its 3:5-dinitrobenzoate proved it to consist mainly of this alcohol. The procedure for the determination of the amount of alcohols was as follows:—The entire contents of a can were passed through a meat chopper three times. A portion of the minced product (50 g.) was made into a uniform suspension with water (100 ml.) and treated with 15 ml. of 2 *N* sulphuric acid and 15 ml. of 20 per cent. phosphotungstic acid, and, after dilution to 250 ml., the mixture was filtered. The filtrate (150 ml.) was mixed with 10 ml. of Denigès' reagent (U.S.P. XI), made up to 200 ml. and distilled in an all-glass apparatus until 100 ml. of distillate had been collected. The distillate was treated with 5 ml. of Denigès' reagent and with a suspension of lime (100 g. of calcium oxide in 1 litre of water) until the mixture became orange. After dilution to 150 ml. the mixture was distilled and 100 ml. of the distillate were collected. An aliquot portion of the distillate was treated with 10 ml. of 5 *N* sodium hydroxide solution and 25 ml. of 0·02 *N* potassium permanganate solution and heated on the water-bath for at least 20 minutes. When cold, the liquid was acidified with 10 ml. of *N* sulphuric acid, and sufficient potassium iodide was added to react with the unaltered permanganate. Finally, the liberated iodine was titrated with 0·02 *N* sodium thiosulphate solution. Each ml. of 0·02 *N* potassium permanganate solution is equivalent to 0·0855 mg. of ethyl alcohol. The aliquot portion of the distillate should be such that not more than 6 ml. of potassium permanganate solution are required. Usually 25 ml. is a suitable aliquot portion, but if a smaller aliquot portion is taken, the volume in the reduction flask should be adjusted with water to 60 to 70 ml. The reaction is not linear, but gives consistent results if the conditions of time, volume and concentration of alkali are as stated. A. O. J.

Volatile Fatty Acids as an Indication of Spoilage in Canned Sardines. F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 414–418.)—Previous work (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 684; 1938, **21**, 688; Abst., ANALYST, 1939, **64**, 44; 1939, **22**, 116) on the determination of volatile fatty acids in canned salmon, tuna fish and herring roe is now extended to include canned sardines, the volatile fatty acid number and formic acid number being determined by the method previously described (Abst., ANALYST, *loc. cit.*). When prepared from the freshest materials, canned sardines contain a small amount of volatile acids, and this amount increases progressively as decomposition proceeds. Four samples prepared from authentic material and representing stages of spoilage from fresh to badly decomposed gave the following figures:—formic acid number, 1·2 to 1·8, 1·5 to 1·8, 3·3 to 6·0 and 15·5 to 21·1; volatile fatty acid number, 15·8 to 18·6, 21·6 to 24·5, 57·1 to 80·8, and 156·1 to 201·5. With fish packed in sauce (especially in mustard preparations) the volatile fatty acid number has only a limited value as a criterion of freshness, but the formic acid number still serves as a valuable index. The formic acid number of sardines canned in a mustard preparation (1·7 to 2·0) did not differ greatly from that of the same fish packed without sauce (1·5 to 1·8), but when the fish were packed in tomato sauce the number was slightly higher (2·1 to 3·2). Attempts were made to identify the individual acids present. From a study of the fractional distillation curves it was concluded that the highest detectable member of the series present was propionic acid with possibly traces of one or more higher members of the series. A. O. J.

Grading Milk by the Resazurin Test. J. G. Davis. (*Food Manufacture*, 1939, **14**, 196–198, 207.)—Resazurin is a blue dyestuff which is prepared by the interaction of resorcinol and nitric acid containing nitrous acid. It is an oxidation-reduction indicator (range, +0·18 to +0·09 volt), and on reduction it is first converted irreversibly into the pink resorufin and then, reversibly, into the colourless di-hydroresorufin. Both resazurin and resorufin are indicators of acidity, the former being blue at *p*H 6·5 and red at *p*H 5·3, and the latter pink at *p*H 6·5 and yellow at *p*H 4·8. Since the oxidation-reduction range of methylene blue is +0·12 to +0·03 volt, and the normal redox-potential of fresh milk is just over +0·2 volt, it is evident that very weak reducing systems in milk, irrespective of their origin, will affect resazurin much more than methylene blue. Although as a consequence resazurin is reduced more rapidly, and therefore enables a result to be obtained more quickly than with methylene blue, it is sensitive to reducing systems other than those that reduce methylene blue in milk (*cf.* Hobbs, *J. Dairy Res.*, 1939, **10**, 35); examples of the latter are the effects of bacteria such as *Coli aerogenes*, lactic acid streptococci and staphylococci, which in the logarithmic phase of growth may rapidly reduce the redox-potential of milk from +0·2 to less than —0·2 volt. Although non-bacterial factors (*e.g.* reducing enzymic systems) may influence the rate of reduction of methylene blue in milk, the actual reduction itself is invariably due to bacterial development. A fair degree of correlation exists in fact between the bacterial-content of milk and the rate of reduction of methylene blue, because, although only some of the bacteria present initially are responsible for the final reduction, on an average these are a reasonably constant proportion of the entire flora. In special circumstances, however, and particularly when high cell-counts (*e.g.* due to mastitis) are obtained, almost complete reduction of methylene blue by a fresh sample of the milk may occur immediately, although the colour may return after about 30 minutes, after which true reduction occurs (*cf.* McClemont and Davis, *id.*, 1939, **10**, 88). Nevertheless, as a test for bacterial count resazurin is inferior to methylene blue; it has a greater susceptibility to the weakly-reducing systems associated with them, and the fact that it is more rapid in action does not compensate for the resulting loss in accuracy. The value of resazurin depends on the fact that it is more sensitive to the weakly-reducing systems of the cells (leucocytes and tissue cells), and therefore it is more responsive to mastitis; thus it is likely to be of more interest to manufacturers for the control of milk-processing and especially for cheese-making (*cf.* Davis and McClemont, *id.*, 1939, **10**, 94) than to those concerned with the liquid milk market; where the bacterial count is the primary concern the methylene blue test should be used. The procedure for the test is similar to that of the methylene blue test (*cf.* Davis, *Dairy Ind.*, 1939, **3**, 214, 25; 1939, **4**, 83). The resazurin should be of good quality, as some samples on the market are of no use; the author used Eastman's product. A graduated test-tube is filled to the 10-ml. mark with the sample, under aseptic conditions, the mouth of the sample-bottle and of the test-tube being "flamed." One ml. of a 0·0005 per cent. solution of resazurin is added, and the tube is closed, inverted twice, and placed in a bath at 37° C. Resazurin is sensitive to light, and both the tubes and the stock 0·05 per cent. solution from which the reagent is prepared should be kept in the dark (the latter in a refrigerator). On reduction the colour normally changes from blue, through mauve and pink to colourless, and the results may therefore be recorded in terms of the colour after a definite period (*e.g.* 1 hour), or as the time required to produce a definite colour. The pink shade is usually sufficiently distinct for the latter purpose and the time to attain this is 75 per cent. of that required for complete decolorisation (*cf.* Johns, *Amer. J. Pub. Health*, 1939, **29**, 239); moreover, it is this earlier stage of reduction which corresponds most closely with the effects of non-bacterial reducing systems. The advantages of the first method, however, are that it enables the test to be completed in 1 hour, and it allows compensations for changes in temperature to be made more easily. It is further facilitated by means of colour standards painted on cardboard. The scale suggested is:—(1) Blue, excellent; (2) slightly mauve, very good; (3) mauve, good; (4) pink-mauve, fair; (5) mauve-pink, poor; (6) pink and (7) colourless, bad. These assessments refer to both bacterial quality and freedom from pathological abnormality. It is recommended that three tests should be made on each sample, and that when two or all of these give results corresponding with standards, 5, 6 or 7, a direct microscope test should at once be made, *e.g.* by staining a smear of the milk with polychrome or Loeffler's methylene blue (*cf.* Barrett and others, *J. Dairy Sci.*, 1937, **20**, 705; and Jenkins, *id.*, 1938, **21**, 141). The reduction of dyestuffs in milk may be influenced by factors other than bacteria, *e.g.* the breed of the cow, the season of the year, and the fat-content; further investigations on these influences are desirable. J. G.

Detection of Glucose Syrup in Honey by the "Acetic Acid Method." P. N. Raikow. (*Z. anal. Chem.*, 1939, **117**, 100–102.)—The presence of glucose syrup in honey has been detected (Raikow, *Z. anal. Chem.*, 1939, **116**, 40) by the formation of a white turbidity on pouring 1 ml. of glacial acetic on to about 5 g. of the honey in a test-tube. This turbidity, which may appear immediately or may be delayed, in the upper, acetic acid layer is caused by the dextrin of the glucose syrup. It was found that on allowing the test-tube to stand for some time the turbidity gradually decreased and finally disappeared, leaving a clear liquid. Recent experiments indicate that this is due to the absorption of atmospheric moisture by the acetic acid; with honey containing 10 per cent. of glucose, acetic acid containing more than 3 per cent. of moisture forms no turbidity even after long standing. With 97 per cent. acid a dense white turbidity appears; with 98 and 99 per cent. acid the turbidity is denser and almost as great as that with anhydrous glacial acetic acid. The reaction occurs more rapidly and is more pronounced if, after addition of acetic acid, the test-tube is warmed for a short time in the boiling water-bath and then allowed to cool without shaking. As honey is only slightly miscible with glacial acetic acid and the reaction therefore occurs only at the surface of contact, 5 g. are not required and even 1 to 2 g. are sufficient for the test. One gram of a 50 per cent. solution of pure glucose syrup in water gives a white turbidity with 4·5 ml. of glacial acetic acid; this disappears on warming the mixture, but re-appears on cooling. With less acid a curdy white precipitate is formed at the surface of the solution but disappears on shaking. The following modification of the original test is now proposed:—To about 5 ml. of acetic acid in a test-tube one drop of honey is added with a glass rod, the mixture is heated, with shaking, in a boiling water-bath and then cooled. If a white turbidity appears the test can be repeated several times by the addition of further drops of honey. The turbidity becomes denser each time until the limiting solubility of the glucose syrup in acetic acid is reached, after which further addition of honey causes the acid gradually to become clear; it again becomes turbid on addition of more acetic acid. By this modification of the test very small amounts of honey can be used, and by diminution of the acid used the very smallest amounts of glucose syrup can be detected. E. B. D.

Green Turtle Oil. C. Hata. (*J. Soc. Chem. Ind., Japan,* **1939, 42,** 88B.)—The present sample of oil from the green turtle, *Chelonia japonica* (Thunberg) was pure body oil, free from liver oil; the yield was about 1·6 per cent. The oil was reddish-orange, gave a considerable deposit at ordinary temperature, was soluble in acetone, and gave hardly any reaction in the antimony trichloride test. It had the following characteristics: sp.gr. at 30/4° C., 0·9127; n_{D}^{30}, 1·4649; saponification value, 210·3 ; iodine value, 80·08; acid value, 1·0; unsaponifiable matter (mainly cholesterol and oleyl alcohol), 1·3 per cent. The fatty acids were liquid at 32° C., and had sp.gr. at 40/4° C., 0·8788; n_{D}^{40}, 1·4512 neutralisation value, 213·62; iodine value 81·79. The yield of ether-insoluble bromide was 3·2 per cent. with bromine-content 66·11 per cent., and the yield of bromide insoluble in petroleum spirit was 1·0 per cent. with a bromine-content of 59·58 per cent. The following acids were identified: zoomaric, oleic, an isomer of linolenic acid, $C_{18}H_{30}O_2$, a small quantity of clupanodonic, and a new highly unsaturated acid, $C_{26}H_{44}O_2$, called chelonic acid; this had neutralisation value, 141·26; iodine value, 258·05; it yielded an insoluble bromide, m.p. 248–250° C., containing 61·75 per cent. of bromine. (*Cf. J. Soc. Chem. Ind. Japan,* 1937, **40,** 185B; Abst., ANALYST, 1937, **62,** 619; *Biochem. J.*, 1938, **32,** 681; Abst., ANALYST, 1938, **63,** 442; also ANALYST, 1935, **60,** 650). D. G. H.

Okigisu Fish Oil (*Argentina kagoshimae,* Jordan and Snyder). S. Ueno and T. Tamura. (*J. Soc. Chem. Ind., Japan,* 1939, **42,** 150–151B.)—Okigisu is a small fish widely distributed in Japanese waters. Two samples of oil, of a reddish-orange and reddish-brown colour respectively, had the following characteristics:—sp.gr. at 15/4° C., (*a*) 0·9226, (*b*) 0·9229; n_{D}^{20}, (*a*) 1·4760, (*b*) 1·4743; saponification value, (*a*) 186·0, (*b*) 188·8; iodine value, Wijs, (*a*) 148·3, (*b*) 150·7; acid value, (*a*) 47·8, (*b*) 9·5; unsaponifiable matter, (*b*) 2·45 per cent. The mixed fatty acids from sample (*b*) had m.p. 31·0–32·5° C., iodine value, 161·7, and neutralisation value, 191·6. Separation by the lead salt and alcohol method gave 18·5 per cent. of solid acids with m.p. 51·3–52·2° C.; iodine value, 8·9; neutralisation value, 213·2; liquid acids, 81·5 per cent., with iodine value 194·8 and neutralisation value, 188·1. About 580 g. of solid acids were methylated and fractionally distilled, and an examination of the fractions revealed the presence of myristic, palmitic, stearic, behenic and tetracosanic (probably *n*-tetracosanic) acids, with palmitic acid as the main constituent (about 60 per cent.). D. G. H.

Chemical Examination of the Wax from Sugar Cane. N. L. Vidyarthi and M. Narasingarao. (*J. Indian Chem. Soc.*, **1939, 16, 135–143.**)—The wax isolated from the press cake from a sulphitation factory treating sugar cane had the following characteristics: m.p. 68·7° C.; saponification value, 133·5; iodine value, 31·5; acid value, 23·4; acetyl value, 89·6; unsaponifiable matter, 43·7 per cent. It consisted of 53·0 per cent. of acids which were examined by the ester fractionation method of Hilditch, and found to comprise resin acid, 4·5; caproic, 0·6; palmitic, 27·7; stearic, 22·4; oleic, 41·5; arachidic, 3·3 per cent. The unsaponifiable part of the wax (43·7 per cent.) was treated by the phthalic anhydride method of Chibnall *et al.* (*Biochem. J.*, 1931, **25**, 2095; Abst., ANALYST, 1932, **57**, 258) and was resolved into primary and secondary alcohols and paraffins. The main portion (about 80 per cent.) was the primary myricyl alcohol, and about 10 per cent. consisted of a mixture of sterols, which by conversion into acetates and fractional crystallisation of the brominated products (Windaus and Hauth, *Ber.*, 1906, **39**, 4378) was found to contain brassicasterol, stigmasterol and sitosterol. About 5 per cent. of an aliphatic paraffin, *n*-pentatriacontane ($C_{35}H_{72}$), was separated but no dibasic or oxyacids could be detected. D. G. H.

Manganese-content of Indian Foodstuffs and Other Materials. M. N. Rudra. (*J. Indian Chem. Soc.*, 1939, **16**, 131–134.)—The manganese content of a number of Indian foodstuffs and some other materials has been determined by the Skinner and Petersen method (*J. Biol. Chem.*, 1930, **88**, 347; Abst., ANALYST, 1930, **55**, 640) with modifications where found necessary, and also in two instances by the Richards' method (ANALYST, 1930, **55**, 554). The manganese present in typical plant materials (mg. per 100 g. of dry substance) was: rice, sundried and polished, 1·34; parboiled, 1·96; wheat, 2·07; green gram, 1·93; Bengal gram, 3·00; cabbage, 5·69; amaranth, tender, 6·37; mature, 5·86; carrot, 0·754; knol-khol, 5·21; cauliflower, 2·62; brinjal, 2·40; guava, 1·59; chillies, green, 1·64; jujuba plum, 0·982; Indian gooseberry, 2·90. For animal products the figures were:—goat: liver, 1·233; muscle, 0·07; rohit fish: muscle, 0·248; scales, 8·831; calbosh fish muscle, 0·243; mrigal, catla and chital fish muscle, 0·2; milk, 0·0075 per 100 ml.; cows' milk, 0·006 per 100 ml. The plant products rich in manganese are also usually rich in vitamin C and *vice versa*, and the fact that the manganese-content of living materials runs almost parallel with their vitamin C content is illustrated by the figures for (*a*) tender and (*b*) mature amaranth leaves: manganese (mg. per 100 g. dry substance), (*a*) 6·37, (*b*) 5·86, vitamin C content (mg. per 100 g. of moist substance):—(*a*) 151, (*b*) 140. D. G. H.

Photometric Determination of Nicotine on Apples without Distillation. L. N. Markwood. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 427–436.)—By the method previously described (*J. Assoc. Off. Agr. Chem.*, 1938, **21**, 151; Abst., ANALYST, 1938, **63**, 288), the nicotine on apples sprayed with nicotine bentonite is determined by distillation and conversion into the silicotungstate. The colour test for the determination of pyridine described by Barta (*Biochem. Z.*, 1935, **277**, 412) and shown later by Barta and Marschek (*Mězogazdasagi Kutatasok*, 1937, **10**, 29) to be applicable, but with less sensitivity, as a test for nicotine can be used for the direct determination of nicotine on sprayed apples. The reagents are cyanogen bromide solution (freshly prepared by the addition of 10 per cent. potassium cyanide solution to saturated bromine water until it is decolorised and dilution of the product with water to five times its original volume), and a freshly prepared solution of 0·2 g. of *β*-naphthylamine in 100 ml. of 95 per cent. alcohol. This solution should not be exposed to sunlight, but a moderate fluorescence in daylight is normal. To prepare the standard comparison curve, 0·4 g. of nicotine bentonite is shaken with 400 ml. of 0·5 per cent. sodium hydroxide solution, 400 ml. of water and 20 ml. of calcium acetate solution containing 4 g. of calcium per litre. The calcium compound serves to convert the bentonite into "calcium bentonite" which, unlike bentonite, is readily separated by filtration. The mixture is diluted to 1 litre, allowed to stand for 15 minutes and filtered. Aliquot portions of the filtrate (usually 50, 100, 150 and 200 ml.) are adjusted to the same alkali content as the largest by the addition of appropriate amounts of sodium hydroxide solution and, after the addition of phenolphthalein, the solutions are nearly neutralised with 30 per cent. acetic acid. Dilute acetic acid (2 per cent.) is then added until the indicator is colourless, one drop being added in excess. By this procedure the concentration of sodium acetate and the *p*H of the solution are fixed at the optimum values for the development of the colour. The solutions are diluted to 250 ml., and a 5-ml. portion of each solution is treated with exactly 1 ml. of cyanogen bromide solution, and, after mixing, with exactly 5 ml. of β-naphthylamine solution. The mixtures are placed in the dark for an hour, after which photometric measurements of the red or pink colour are made and a standard curve is constructed showing the relationship between the photometric reading and the concentration of nicotine. In accordance with Beer's law, a straight line was obtained for the range investigated, *viz.* 0 to 16γ. To determine the nicotine on sprayed apples, the fruit (about 10 mature apples) is shaken in a closed vessel first with 200 ml. of sodium hydroxide solution, then with 180 ml. of water, and finally with 80 ml. of water. The extracts are mixed, and 0·2 g. of powdered bentonite and 10 ml. of calcium acetate solution are added. The mixture, diluted to 500 ml., is filtered, and an aliquot portion (200 ml.) is treated as described for the standard solutions. The amount of nicotine present is determined from the curve. Lead arsenate, calcium arsenate, Bordeaux mixture, copper ammonium silicate, and "wettable sulphur" do not interfere with the process, but if cryolite is present, it is necessary to remove the fluoride ion from the alkaline solution by filtration after treatment with calcium oxide. Lime-sulphur caused the most interference of all added substances, the recovery of nicotine being only 86 per cent. when all forms of sulphur had been removed from the solution. It appears necessary in this instance to separate the nicotine by distillation before applying the method. Among organic compounds that may be present pyridine answers to the test, but its presence is unlikely, owing to its volatility. Its homologues respond only very feebly to the test. Nicotinic acid, which may be formed by oxidation of the nicotine, is removed as an insoluble calcium salt. Hitherto the method has been applied only to recently picked apples, and it is not claimed that the extraction will be equally complete with apples which have formed a thick coating of wax during storage. The accuracy of the method was tested by adding known amounts of nicotine bentonite to unsprayed apples. With a neutral wedge photometer equipped with a 10-cm. tube and a monochromatic filter transmitting around 490$m\mu$, it was found possible to determine a nicotine concentration of 1 part in 4 millions in the final solutions. Determinations were made of the nicotine on single apples (about 0·8 mg.). A. O. J.

Identification of Strophanthus Species and their Tinctures. P. Dumont and G. Thomas. (*J. Pharm. Belg.*, **1939, 21,** 397–402.)—The commercial species of *Strophanthus* are three: (*a*) *S. kombe* from the East Coast of Africa, (*b*) *S. hispidus* from the West African French Possessions, and (*c*) *S. gratus* or *glaber* from the Cameroons and Gaboon. In Belgium (*a*) and (*b*) are official, but (*c*) is used in other countries. The seeds of *S. gratus* may be distinguished from those of *S. kombe* and *S. hispidus* by being free from hairs, but magnification is necessary to distinguish between the long silky hairs of *S. kombe* and the short and close-set hairs of *S. hispidus*. The reactions given in the literature usually refer to *S. kombe* and *S. gratus*, whilst *S. hispidus* is ignored (*cf.*, however, Smelt, *Pharm. J.*, 1933, **131**, 150–151; Abst., ANALYST, 1933, **58**, 704). Of the various distinguishing reactions investigated, that with furfural and sulphuric acid, and with vanillin in hydrochloric acid were found to be the most satisfactory and were studied in detail. In the former both *S. hispidus* and *S. kombe* tinctures give an indigo-blue colour which develops rapidly, and in proportion to the quantity of acid used, whilst *S. gratus* under similar conditions gives only a feeble rose colour, slowly intensifying towards violet. To distinguish *S. kombe* from *S. hispidus* the fluorescence, in ultra-violet light, of the ethereal solutions from the de-fatting of the powder preparatory to making the tincture may be examined. *S. kombe* shows an orange-red, *S. gratus* a quinine blue, and *S. hispidus* a pale lilac fluorescence. For the examination of tinctures, the alcohol is first completely evaporated on a water-bath, and the aqueous residue, after cooling, is shaken with 3 ml. of ether. The ethereal solution is shaken with 10 ml. of 0·1 *N* sodium hydroxide solution, and after separation of the two layers (by centrifuging if necessary), the aqueous layer is examined in ultra-violet light; *S. kombe* gives a blue, and *S. hispidus* and *S. gratus* a yellow-green fluorescence. D. G. H.

Biochemical

Nutritive Value of Wheaten Products. N. Palmer. (*Biochem. J.*, 1939, **33**, 853–858.)—The nutritive value of a mixed wheaten product consisting of 3 parts of wheat flour and 1 part of added germ was tested on a colony of albino rats. The abnormal calcium/phosphorus ratio (1 : 9) of the mixture was adjusted by addition of 3 per cent. of calcium lactate to produce a calcium/phosphorus ratio of 1:0·45. This modification effected a marked improvement in the nutritive value of the mixture, and a first generation of rats was reared and brought to sexual maturity on it. Some of the animals produced litters and in some instances suckled their young. This second generation was in turn reared on the diet and enabled to breed, but a third generation could not be reared on it. Adjustment of the calcium/phosphorus ratio of ordinary white flour did not remedy its lack of nutritive value. The flour-germ mixture with added calcium was superior to a meat diet with added calcium. A diet of bread and milk or bread and cheese gave excellent results, and rats fed on it grew rapidly and produced several litters.

F. A. R.

Enzyme Activity in Frozen Vegetables. Stringbeans. C. M. Bedford and M. A. Joslin. (*Ind. Eng. Chem.*, 1939, **31**, 751–758.)—The investigation recorded was undertaken with the object of ascertaining the minimum temperature necessary in "blanching" stringbeans to destroy the enzymes, which otherwise give rise to unpleasant flavours on storage even at −17° C. The activity of catalase, peroxidase and ascorbic acid oxidase and the acetaldehyde-content were studied. It was found that acetaldehyde, a known product of anaerobic respiration, accumulates in samples containing active catalase. The amount of acetaldehyde decreases with catalase activity, but there is no definite relation between the two, such as was found for peas, and the amount of the former and the activity of the latter are not a reliable index of flavour retention. The rate of heat inactivation of catalase was found to be more rapid than that of the agencies producing the flavours. The ascorbic acid oxidase activity runs closely parallel with that of catalase and is inactivated by heat at about the same rate. The peroxidase activity, as measured by the rate of decomposition of hydrogen peroxide in the presence of pyrogallol, is more resistant to heat, and there is close correlation between its inactivation and the keeping quality. It is difficult, however, to determine definitely from the data obtained how much of the peroxidase must be destroyed in order to secure good keeping quality; apparently it need not all be destroyed. The temperatures for "blanching" employed varied from 55° to 100° C., and the time from 30 seconds to 1 hour; the effect of these exposures upon the enzymes is recorded. A satisfactory product was obtained by "blanching" cut stringbeans for 2 minutes at 85° to 87·5° C., or for 5 minutes at 82·2° C., and for 2 minutes at 100° C. with less mature uncut stringbeans. D. R. W.

Effect of Calcium Ion on Tissue Respiration, with a Note on the Estimation of Oxaloacetic Acid. G. D. Greville. (*Biochem. J.*, 1939, **33**, 718–722.)—The inhibitory effect of calcium ions on the respiration of minced muscle is not localised in any particular enzymic reaction, since both the formation and removal of oxaloacetic acid, and also the accumulation of succinic acid, were shown to be inhibited by the presence of calcium ions. The experiments by which this was demonstrated required a method of estimating oxaloacetic acid. In Ostern's method (*Z. physiol. Chem.*, 1933, **218**, 160) the carbon dioxide evolved when aniline reacts with oxaloacetic acid is measured in a Warburg apparatus, but the reaction is slow, since it has to be carried out at 5° C. to avoid decomposition of the acid prior to reaction with aniline. Two methods were used to increase the rate of reaction. In the first method aniline citrate was employed—a reagent previously used by Edson (*Biochem. J.*, 1935, **29**, 2082) in the estimation of acetoacetic acid at 25° C. The aniline citrate solution is added to the oxaloacetic acid solution from the side-bulb at 5° C., and the reaction is complete in 10 to 20 minutes. A correction has to be applied for the solubility of carbon dioxide in the mixture in the vessel. Duplicate estimations differed by not more than 2·5 per cent., and 97 per cent. purity was indicated by the method for three different oxaloacetic acid preparations. In the second method the bulb contains 0·2 ml. of aniline previously mixed with 0·15 ml. of conc. hydrochloric acid, whilst the main part of the apparatus contains a mixture of 1·5 ml. of absolute alcohol, 0·3 ml. of acetate buffer solution (0·3 N sodium acetate solution and 2·7 N acetic acid) and 0·86 ml. of the solution to be analysed. Again, a correction must be applied for the solubility of carbon dioxide. Results were obtained agreeing closely with those given by the first method. Whereas the alcohol method does not distinguish between oxaloacetic acid and acetoacetic acid, the citrate method at 5° C. does, and oxaloacetic acid can be estimated in the presence of acetoacetic acid. The evolution of carbon dioxide from the latter is slow and fairly constant, and extrapolation to zero time gives the amount of oxaloacetic acid with reasonable accuracy. F. A. R.

Fermentation Process in Tea Manufacture. I. Rôle of Peroxidase. E. A. H. Roberts and S. N. Sarma. (*Biochem. J.*, 1938, **32**, 1819–1828.)—The processing of tea is briefly as follows:—After plucking, the tea-leaf is first spread out in thin layers to undergo withering, and is then subjected to a rolling process, the primary purpose of which is to rupture the leaf-cells and expose the expressed juices to the air. At the same time the tea receives its characteristic twist. It is at this stage that fermentation begins, and after 1½ hours' rolling fermentation is continued on the fermenting floor for a further 2 hours, after which the tea is fired to stop fermentation and dry the leaf. It is now certain that the process of fermentation is an oxidation by atmospheric oxygen catalysed by peroxidases in the leaf. The first stage is an uptake of oxygen leading to the oxidation of some as yet unidentified substance and the production of hydrogen peroxide. The peroxidase then catalyses the oxidation of the tea tannin by means of this hydrogen peroxide, leading to the production of brown pigments which impart the characteristic colour to a tea infusion. The "non-tans" (*i.e.* matter oxidised by potassium permanganate, but not precipitated by gelatin and acid salt) also appear to undergo oxidation during fermentation. No evidence could be obtained that organic peroxides are utilised by the peroxidase in place of hydrogen peroxide. Tea tannin inhibits peroxidase action, but substances present in the leaf exert some protective influence against its effects. The authors devised a method of estimating peroxidase activity in tea-leaf, based on that of Guthrie (*J. Amer. Chem. Soc.*, 1931, **53**, 242; Abst., ANALYST, 1931, **56**, 194). A solution of 1·05 g. of crystalline citric acid in 8·5 ml. of N sodium hydroxide solution was diluted to 100 ml. with water, and 0·25 g. of *p*-phenylenediamine hydrochloride and 5 ml. of a 4 per cent. solution of α-naphthol in 50 per cent. alcohol were added. The solution was then filtered. Ten ml. of this reagent were mixed with the enzyme solution (2 ml.) and 2 ml. of 0·05 N hydrogen peroxide solution were added. After 10 minutes' incubation the reaction was stopped by the addition of 2 ml. of 1 per cent. potassium cyanide solution. An aliquot portion (usually 3 ml.) was extracted with 25 ml. of toluene, and the colour of the toluene layer was measured in a Lovibond tintometer (red and blue glasses). A solution was said to have 6 Indophenol units (I.U.) when the total reading of the red and blue slides was 6·0. The peroxide-content of an unknown solution was calculated from a calibration curve. Since peroxidase activity is inhibited by tannins, the latter have to be removed before the estimation can be carried out. The leaf sample (10 g.) was therefore ground with sand under alcohol, the alcoholic suspension was filtered, and the residue was washed, dried and extracted with 100 ml. of $M/15$ phosphate buffer solution (*p*H 7·0). The method was employed to follow the variations in peroxidase-content that occur during the process of manufacture. An increase was found after withering, followed by a marked decrease after the first rolling, with a slight though regular decrease in the second rolling and the fermentation. The firing did not completely destroy the peroxidase, for 0·5 to 1 per cent. of the original activity remained. This may be of some importance in the post-fermentative changes that take place on maturing. F. A. R.

Fermentation Process in Tea Manufacture. II. Some Properties of Tea Peroxidase. III. Mechanism of Fermentation. E. A. H. Roberts. (*Biochem. J.*, 1939, **33**, 836–852.)—II. The peroxidase-content of fresh tea leaves, estimated by the method previously described (*cf.* preceding abstract), was found to vary widely in single shoots (and even in different parts of a shoot) from the same bush and in samples from different bushes on the same plot. Representative samples showed regular variations in the peroxidase activity from week to week. In the curve in which these variations were plotted, three well-defined regions were observed, corresponding closely with three quite sharply contrasted types of tea. Little correlation, however, was found between peroxidase activity and the rate of fermentation (peroxidase-catalysed oxidation of tannin); this suggests that peroxidase is not the sole factor governing the rate. The peroxidase activity was found to increase during the withering process and was accelerated by loss of moisture until a critical level (72 per cent.) was reached, after which there was a decrease. Estimations of the rate of fermentation in fresh and withered leaf were carried out by measuring both the rate of oxygen uptake (see Part III) and the rate of decrease of the tannin titre, and by neither method was any significant difference observed between the fermentation rates for green and for withered leaf. Protein nitrogen was found to decrease during withering. As the rate of oxidation of tannins appears to be quite independent of the peroxidase activity, it is concluded that the oxidation is preceded by a relatively much slower reaction in which hydrogen peroxide is formed, and that the rate of fermentation depends on the rate of hydrogen peroxide formation. It is further suggested that the hydrogen peroxide required is derived from oxidation of the "non-tans" during fermentation. The proposed mechanism of fermentation can thus be represented by the equations:

$$(1)\ \text{"Non-tan"} + O_2 \longrightarrow \text{oxidised "non-tan"} + H_2O_2.$$

$$(2)\ H_2O_2 + \text{tea tannin} \xrightarrow{\text{peroxidase}} \text{oxidised tea-tannin}.$$

III. Estimations of the rates of oxygen uptake by fermenting tea-leaf were made by the Barcroft-Warburg method, 200 mg. of the finely-minced leaf being suspended in 3 ml. of water and the reaction vessel shaken vigorously in a thermostat maintained at 35·5° C. The uptakes were the same over a *p*H range of 4·6 to 6·6 and were initially quite rapid, but fell off when the substrate was exhausted. At this stage about 80 per cent. of the original enzyme activity was still present. Carbon dioxide was also produced during fermentation, presumably by oxidation of carbohydrate. After allowance had been made for the oxygen required in the latter reaction, it was calculated that one atom of oxygen is required for the complete oxidation of one molecule of tea tannin. Since carbon dioxide was produced in amounts equivalent to about half the total oxygen uptake, it seemed probable that the "non-tans" oxidised during fermentation were carbohydrates, and this was confirmed by the identification of glucose as the major constituent in a tannin-free extract of the "non-tans." Estimations of the ascorbic acid content of green leaf were made, after removal of tannin with neutral lead acetate, by titration with 0·01 *N* iodine solution after the addition of 4 ml. of 12 *N* sulphuric acid. It was found that 1 g. of fresh green leaf contains about 1 mg. of ascorbic acid. A thermolabile catalyst of ascorbic acid oxidation appears to be present in the leaf. The addition of ascorbic acid to fermenting leaf had no effect on the rate of oxygen uptake, but the rate was maintained for a longer period, the ascorbic acid being oxidised before either the tannin or the carbohydrate is attacked. Since, however, the rate of oxygen uptake during the oxidation of ascorbic acid is identical with the rate of normal fermentation, it is evident that the latter is controlled by the former. This, however, is the same as the rate of production of hydrogen peroxide, which is required for the peroxidase-catalysed oxidation of tannin. A shortage of ascorbic acid oxidase, as occurs in Kharikatia leaf, results in a slower rate of fermentation. The dehydroascorbic acid formed by oxidation of ascorbic acid probably serves as a hydrogen acceptor during the oxidative breakdown of carbohydrate, ascorbic acid being regenerated only to be re-oxidised and the cycle repeated. About 20 moles of tea tannin are oxidised for each mole of ascorbic acid present. The primary product of tannin oxidation is probably an *o*-quinone which either condenses irreversibly or is again reduced to tea tannin by ascorbic acid. The complete reaction scheme for fermentation can be summarised as follows:

(1) Ascorbic acid + $O_2 \xrightarrow{\text{ascorbic acid oxidase}}$ dehydroascorbic acid + H_2O_2.

(2) H_2O_2 + tea tannin $\xrightarrow{\text{peroxidase}}$ tannin *o*-quinone.

(3) *o*-Quinone $\longrightarrow$ condensation products.

(4) *o*-Quinone + ascorbic acid $\longrightarrow$ tea tannin + dehydro-ascorbic acid.

(5) Dehydroascorbic acid + glucose $\xrightarrow{\text{zymase}}$ CO_2 + ascorbic acid.

F. A. R.

Vitamin G Content of some Oil Presscake Meals and Related Products. F. W. Sherwood. (*J. Agric. Res.*, 1939, **58**, 787–794.)—The term "vitamin G" is used to denote the undifferentiated complex which stimulates growth of rats on a basal ration containing maize starch and extract of rice polishings, but otherwise free from water-soluble vitamins, riboflavin being probably the chief limiting factor of the diet. Peanut, cottonseed, linseed and soya bean meals, as well as cottonseed flour and cottonseed hull bran, and soya beans, were fed to rats previously maintained on the basal ration (devoid of the vitamin B complex) with 2 drops of extract of rice polishings daily until they ceased to gain in weight, and standard yeast was given for comparison to a further batch of rats that had been similarly fed. The optimum test period was found to be about 7 weeks. All the products were found to be good sources of vitamin G, the values ranging from 2·5 to 5·9 Sherman–Bourquin units per gram, which is equivalent to the vitamin G content of cheddar cheese and green leafy vegetables. Time of year and, to a less extent, initial weight of the rat and gain in the depletion period, affected the relation between the gain in weight and vitamin G intake, and a curve of reference with corrections is given. D. G. H.

Biological Estimation of Crystalline Vitamin B_1. K. H. Coward and B. G. E. Morgan. (*Biochem. J.*, 1939, **33**, 658–662.)—Kinnersley and Peters (*Biochem. J.*, 1936, **30**, 985) measured the effect of graded doses of vitamin B_1 by the duration of the cure of "retracted neck" in pigeons, and came to the conclusion that with crystalline vitamin B_1 there was no relation between the effect and the dose. When the effect was measured by the percentage of birds cured, however, the relationship between effect and dose was more satisfactory. The response of pigeons to graded doses of crystalline vitamin B_1 given orally has been re-investigated with the following results:

Expt.	Dose mg.	No. of birds	Birds cured Per Cent.	Average duration of cure Days
a	5·0	15	33·3	3·6
	10·0	15	66·7	4·3
b	4·5	22	54·5	6·6
	9·0	22	81·8	5·5
	13·5	22	90·9	6·2
c	3·0	22	59·1	6·2
	6·0	22	50·0	8·7
	9·0	22	77·3	7·4
d	1·0	25	8·0	5·5
	3·0	25	28·0	5·6
	9·0	25	56·0	5·4

From the above table it is clear that there is a direct relationship between the dose and the percentage of birds cured, but not between the dose and the duration of cure; this confirms the earlier work of Kinnersley and Peters. The accuracy of the method is greater, the larger the number or birds used, the more nearly the number of birds cured approaches 50 per cent., and the steeper the response curve. Statistical examination of the results shows that the pigeon method of assay is the least accurate of those investigated by the Sub-Committee on the Accuracy of Biological Assays, British Pharmacopoeia Commission. F. A. R.

Bacteriological

Carbon Monoxide in Underground Atmospheres. The Role of Bacteria in its Elimination. G. W. Jones and G. S. Scott. (*J. Ind. Eng. Chem.*, 1939, **31**, 774–778.)—Tests are described showing that certain types of bacteria occurring in gangway waters, sewage and surface materials are capable of consuming hydrogen and carbon monoxide from gaseous mixtures. The reactions involved appear to be largely oxidation of carbon monoxide to dioxide and of hydrogen to water. In the tests in which oxygen was present in the atmosphere the carbon monoxide did not combine with the hydrogen to form methane and water vapour. Under favourable conditions certain anthracite mine micro-organisms remove carbon monoxide rapidly; one gangway water, for instance, contained sufficient bacteria to remove 1·7 volumes of carbon monoxide per volume of water in 20 days. The types of bacteria to which these reactions are due has not yet been ascertained, but investigations in this direction are in progress.* Experimentally prepared atmospheres containing carbon monoxide and hydrogen were exposed, in a closed glass vessel, to a sponge holding gangway water, and analyses of the mixed gases were made at the beginning of the experiment and after 30 or 40 days. The results obtained in one typical experiment were as follows:

	CO_2	O_2	H_2	CO	CH_4	N_2
Percentage at beginning ..	0·4	11·3	14·3	12·3	0	61·7
,, after 30 days ..	7·0	4·7	1·6	7·6	0	79·1

It is suggested that it is unsafe to assume that anthracite mine fires are extinguished when the atmosphere in a sealed fire area contains no carbon monoxide, for this gas may be eliminated as fast as it is generated. D. R. W.

Bactericidal Properties of Commercial Antiseptics. Effect of *p*H. W. A. Bittenbender, E. F. Degering and P. A. Tetrault. (*Ind. Eng. Chem.*, 1939, **31**, 742–744.)—The bactericidal properties of phenylmercuric nitrate, merthiolate, metaphen, mercurochrome, tincture of iodine, phenol, hexylresorcinol and acriflavine were tested under controlled conditions of *p*H against *Staphylococcus aureus* and *B. coli*. Metaphen and mercurochrome could not be adjusted to the desired *p*H values, and acriflavine gave negative results. All the others showed increased potency as the hydrogen-ion concentration of the medium increased. Phenylmercuric nitrate, for example, was effective in a dilution 1 in 10,000 at *p*H 7·0, and at *p*H 3·0 its potency against *Staphylococcus aureus* was increased tenfold. At *p*H 4·0 phenol showed a 25 per cent. increase as compared with its effect at 7·0. The results of the investigation indicate that, except for interfering factors such as increased insolubility or instability, these antiseptics of widely differing types show a definite increase in effectiveness with an increase in the hydrogen-ion concentration. This is in agreement with the findings of Goshorn, Degering and Tetrault in their studies of the phenylalkanoic acids. Experimental results are set out in tabular form. The culture was adjusted to the *p*H of each test before use. The concentrations indicated in the table killed in 10, but not in 5, minutes at 37° C. In the following abridged table the lowest killing concentrations at extreme *p*H values are shown.

	Staphylococcus aureus		*B. coli*	
	*p*H 3	*p*H 7	*p*H 3	*p*H 7
Phenylmercuric nitrate..	1 in 100,000	1 in 10,000	1 in 400,000	1 in 30,000
Merthiolate	1 ,, 75,000	1 ,, 10,000	1 ,, 100,000	1 ,, 5,000
Tincture of iodine ..	1 ,, 4,000	1 ,, 1,000	1 ,, 4,000	1 ,, 1,500
Phenol	1 ,, 90	1 ,, 60	1 ,, 100	1 ,, 75
Hexylresorcinol ..	1 ,, 100,000	1 ,, 3,000	1 ,, 100,000	1 ,, 5,000

Killing dilutions for intermediate values and those for metaphen and mercurochrome at *p*H 10·0 are also shown. D. R. W.

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* It will be of interest to learn whether *B. pantotrophus*, *B. pycnoticus* and *B. oligocarbophilus* are found.—D. R. W.

Water

Reaction of Carbonic Acid with the Zeolite in a Water Softener. Roy E. King and O. M. Smith. (*Ind. Eng. Chem.*, 1939, **31**, 727–8.)—It is shown that as softening by zeolite proceeds there is a gradual decrease of alkalinity, with the formation of hydrogen zeolite, which subsequently exchanges its hydrogen ion with basic ions and thus forms free carbon dioxide and lowers the *p*H of the effluent water. It was noted that no matter how narrow the range of the alkalinity of a water before treatment there was a wide variation in the alkalinity of the effluent from the zeolite filter, and the investigation recorded was consequently undertaken. Two waters of practically the same composition were investigated (full analyses are given); they showed (in parts per 100,000) 20·6 total hardness as $CaCO_3$, 19·0 alkalinity, 1·8 chloride and 3·3 sulphate, but one contained 1·5 part of free carbon dioxide and the other only 0·7. Graphs are given showing the changes in the alkalinity, carbon dioxide content and *p*H of the effluent waters from a zeolite filter at half-hourly intervals for 20 hours. These show at the end of the run:

No. 1 (*original free* CO_2 1·5) alkalinity 17·0, free CO_2 3·5, *p*H 6·6; *No.* 2 (*original* CO_2 0·7) alkalinity 16·0, free CO_2 2·2 and no normal carbonate, whereas at the beginning of the run there was no free carbon dioxide in either water and the *p*H of No. 1 was 7·9. The authors believe that the reactions that occur are as follows:

$$H_2CO_3 + 2\text{Na Zeolite} \longrightarrow Na_2CO_3 + 2\text{H Zeolite}$$

and

$$H_2CO_3 + \text{Na Zeolite} \longrightarrow NaHCO_3 + \text{H Zeolite},$$

and that as softening progresses the hydrogen zeolite reacts with the calcium and magnesium bicarbonates as follows: $Ca(HCO_3)_2 + 2\text{H Zeolite} \longrightarrow CaZ_2 + 2H_2CO_3$. The following experiments were made to check these assumptions. Carbon dioxide gas was passed through distilled water until the *p*H was 6·8. The water was then allowed to percolate through a small quantity of greensand zeolite. The effluent had *p*H 9·0 and contained only carbonate alkalinity to the extent of 21 p.p.m. as sodium carbonate. In a further experiment carbon dioxide was passed through distilled water until the *p*H was lowered to 4·9. When this water was allowed to percolate through the zeolite bed, the *p*H increased to 7·9 and only bicarbonate alkalinity appeared to the amount of 11·0 p.p.10^5 as sodium carbonate. Then when sufficient carbonated distilled water had been passed through the zeolite bed so that no further change occurred, tap water with *p*H 7.5 and a total alkalinity of 19·0 p.p.10^5 was substituted for the carbonated water. The effluent water had *p*H 4·4 after it had been heated and aerated to drive off any carbon dioxide; the formation of hydrogen ions was thus indicated. D. R. W.

Agricultural

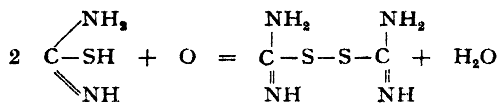
Determination of Thallous Sulphate in Ant Poisons. C. G. Donovan. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 411–414.)—Of the methods available for the determination of thallium, the most applicable to its determination in ant poisons appears to be that based upon its conversion into thallous iodide provided that the conditions are such that the solubility of the precipitated thallous iodide is reduced to a minimum. This compound is slightly soluble in pure water (0·0847 g. per litre at 26° C.), but is much less soluble in solutions of potassium iodide, alcohol or acetic acid and is almost insoluble in water containing ammonia or sodium thiosulphate. A quantity of the sample containing 0·1 to 0·15 g. of thallous sulphate (usually about 10 g.) is heated in a Kjeldahl flask with 25 ml. of conc. sulphuric acid and 5 ml. of conc. nitric acid until the organic matter has been destroyed. The cold liquid is diluted with 10 to 15 ml. of water, washed into a beaker with water until the volume is 60 to 70 ml., boiled for several minutes and filtered, and the filter is washed with hot water until the filtrate measures 175 ml. The filtrate is neutralised with ammonia and, after slight acidification with dilute sulphuric acid, is treated with 1 g. of sodium bisulphite to ensure complete absence of thallic salts. After the addition of 50 ml. of 10 per cent. potassium iodide solution, the mixture is allowed to stand overnight. The precipitated thallous iodide is collected on a Gooch crucible containing two paper discs (S. & S., No. 589) covered with asbestos, and is washed four or five times with potassium iodide solution and finally with absolute alcohol. The crucible is dried to constant weight at 105° C., and the amount of thallous iodide found is calculated to thallous sulphate (factor: 0·7616). The accuracy of the method was proved by the determination of known amounts of thallous sulphate added to such substances as honey, sugar, walnut meal and peat moss in imitation of the commercial products. A. O. J.

Organic

_p_-Xenylsemicarbazide as a Reagent for the Identification of Aldehydes and Ketones. P. P. T. Sah and I. S. Kao. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 459–464.)—*p*-Xenylsemicarbazide gives with carbonyl compounds *p*-xenylsemicarbazones which can be used for the identification of the carbonyl compounds; the reagent allows of the rapid differentiation of normal aliphatic aldehydes from C_2 to C_{10}, which cannot easily be identified by semicarbazones formed from semicarbazide. *p*-Xenylsemicarbazide is prepared by heating under reflux for 24 hours a mixture of *p*-xenylurea, hydrazine hydrate and absolute ethyl alcohol, removing the solvent by distillation, evaporating to dryness, and recrystallising the residue from 95 per cent. ethyl alcohol after washing with ice-cold water. For the identification of aldehydes and ketones, 0·5 g. of *p*-xenylsemicarbazide is dissolved in 5 ml. of 95 per cent. ethyl alcohol, and the solution is acidified with a few drops of glacial acetic acid. A molecular equivalent of the carbonyl compound is dissolved in 5 ml. of 95 per cent. ethyl alcohol, and the solution is added to the semicarbazide solution. The mixture is heated under reflux on the water-bath for a few minutes and filtered hot, and the filtrate is allowed to stand. The semicarbazone generally crystallises out, but if its solubility is too high the solution is concentrated to half the original volume and then allowed to crystallise. The crystals are filtered off with the aid of suction, the m.p. is determined and the crystalline form examined, and the semicarbazone is then recrystallised (usually from 95 per cent. ethyl alcohol, sometimes from ethyl acetate or petroleum spirit) until the m.p. is constant. Tables show the m.p., crystalline forms and nitrogen-contents of a number of *p*-xenylsemicarbazones, and the m.p. of the phenyl-, *p*-tolyl-, *o*-tolyl-, *m*-tolyl- α-naphthyl-, β-naphthyl-, 3·5-dinitrophenyl-, *p*-xenyl-, and 2.4-dinitrophenylsemicarbazones from a number of carbonyl compounds. E. M. P.

β-Naphthazide and β-Naphthyl Isocyanate as Reagents for the Identification of Phenols. P. P. T. Sah. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 453–458.)—Both β-naphthazide and β-naphthyl isocyanate react with phenolic compounds in boiling petroleum spirit to give, almost quantitatively, crystalline urethanes, the properties of which can be used to characterise the phenols. One-hundredth of a mole of β-naphthyl isocyanate (0·17 g.) or an equivalent quantity of β-naphthazide is weighed into an Erlenmeyer flask containing 5 ml. of dry petroleum spirit and an equivalent molecular quantity of the phenol to be tested. The mixture is gently heated under reflux on the sand-bath for 4 hours and then allowed to stand overnight in a cold place; the urethane crystallises out and can be filtered off by suction. The product is weighed, its m.p. determined, and its crystalline form examined. The yield is generally nearly the theoretical. The m.p. becomes constant after 1 or 2 recrystallisations from petroleum spirit. The nitrogen-content of the recrystallised urethane is determined by Kjeldahl's method. Tables give the physical properties and nitrogen-contents of a number of β-naphthyl urethanes in comparison with the m.p. of isomeric α- and β-naphthylurethanes from a number of phenols. E. M. P.

Volumetric Determination of Thiourea. C. Mahr. (*Z. anal. Chem.*, 1939, **117**, 91–94.)—In presence of sufficient potassium iodide, potassium bromate reacts with thiourea according to the equation



$$2\ \overset{\mathrm{NH_2}}{\underset{\mathrm{NH}}{\mathrm{C}}}\!-\mathrm{SH} + \mathrm{O} = \overset{\mathrm{NH_2}}{\underset{\mathrm{NH}}{\mathrm{C}}}\!-\mathrm{S}-\mathrm{S}-\!\overset{\mathrm{NH_2}}{\underset{\mathrm{NH}}{\mathrm{C}}} + \mathrm{H_2O}$$

After this reaction is complete iodine is liberated. In absence of iodide, further oxidation to urea and sulphate occurs before the end of the disulphide reaction. With too high a concentration of iodide, iodine is liberated by the disulphide before the end-point of the titration is reached; hence this is not sharp. The following method for the determination of thiourea is simple and accurate:—The thiourea solution is mixed with 30 ml. of sulphuric acid (1: 1), 5 ml. of 1 per cent. potassium iodide solution and a little starch solution and diluted to about 80 ml.; then, while being shaken round, it is titrated at about 35° C. with $N/10$ potassium bromate solution containing potassium bromide, until a clear blue colour appears. If, after addition of 20 ml. of bromate solution, the reaction is not complete, 1 ml. more of the iodide solution is added. On the appearance of a permanent blue colour the mixture is diluted to 250 ml. with water at about 35° C., which decolorises it, and is then titrated, drop by drop, to the final blue end-point. Test analyses show that the titration can also be carried out in hydrochloric and perchloric acids. Small amounts of nitrate, corresponding with amounts up to about 10 ml. of $2N$ nitric acid, have no effect on the results, but higher concentrations are harmful, as are also copper and mercury salts. Interference by ferric salts is prevented by adding phosphoric acid. E. B. D.

Determination of Tetraethyl Lead in Gasoline. G. Calingaert and C. M. Gambrill. (*Ind. Eng. Chem.. Anal. Ed.*, 1939, **11**, 324–325.)—A 100-ml. sample is heated under a reflux condenser with 50 ml. of conc. hydrochloric acid (sp.gr. 1·19) for 30 minutes. After cooling, the acid layer is separated, the gasoline is washed with 50 ml. of water and the aqueous liquid is evaporated to dryness. Thirty ml. of nitric acid are added to the residual lead chloride, and the liquid is evaporated to dryness to oxidise organic matter. The lead salt is finally dissolved in dilute nitric acid, and the lead is determined by any convenient method: the molybdate titration method with tannin used as external indicator, or the lead chromate gravimetric method, was employed by the authors. With highly volatile gasoline (75 per cent. with b.p. below 100° C.) it is recommended that a 50-ml. sample be used and mixed with 50 ml. of a lead-free sample of higher boiling range (*e.g.* 10 per cent. at 204° C.; 90 per cent. at 238° C.), otherwise the recovery of lead tends to be a little low (by 0·05 to 0·1 ml. of tetraethyl lead per gallon). A convenient all-glass apparatus incorporating an electrical heating unit and separatory funnel is described. S. G. C.

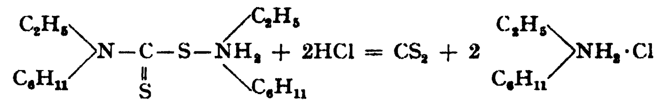
Hydrogenation of Castor Oil with Nickel Catalysts containing Manganese, Zinc or Thorium. K. Kino. (*J. Soc. Chem. Ind., Japan*, 1939, **42**, 189B.)—Castor oil was hydrogenated at a temperature of 200° C. with the following catalysts: (*a*) nickel 10 parts; (*b*) nickel 5, manganese 5; (*c*) nickel 10, zinc 5; (*d*) nickel 10, thorium 5 parts. With nickel alone, iodine and hydroxyl values were much lowered (in 1 hour to 17·8 and 79·5 respectively). Nickel and thorium behaved like nickel alone; the addition of zinc to nickel weakened the hydrogenation of the double bond and reducing action of the ·OH group, whilst with nickel and thorium both actions were stronger than with nickel alone (in 1 hour the iodine value was reduced to 3·2 and the hydroxyl value to 46). D. G. H.

Temperatures of Crystalline Deposition of Stearone and Carnauba Wax from their Solutions in Various Organic Liquids. K. Kino. (*J. Soc. Chem. Ind. Japan*, 1939, **42**, 186–187B.)—Stearone, m.p. 87–88° C., prepared from pure stearic acid and recrystallised from butyl alcohol, and carnauba wax, m.p. 84–85° C., purified by solution in benzene and treatment with activated charcoal, were dissolved in a wide range of organic liquids in the proportion of 0·2, 0·4, 1·0, 2·0, 4·0, 6·0 and 10 per cent., and the temperatures of crystalline deposition were noted. Results were similar for both substances, although, on the whole, stearone was less soluble than carnauba wax. The lowest deposition temperatures were obtained with aromatic hydrocarbons, chloroform and carbon tetrachloride solutions, the next lowest with turpentine oil, hydro-aromatic hydrocarbons, cyclic ketones and acetic esters, and the highest with dibutyl phthalate, castor oil and ethyleneglycol monoethylether acetate. A full table of results is given. D. G. H.

***Cochlospermum tinctorium*, A. Rich. J. Rabaté.** (*J. Pharm. Chim.*, 1939, **29**, 582–583.)—The roots of this member of the *Bixaceae* family, which occurs in the dry regions of French East Africa, are used locally as a source of colouring matters. The samples examined by the author consisted of friable fragments of large rhizomes (length, 10 cm., diameter 4 to 5 cm.) and finer disc-shaped pieces (diameter 2 to 4 cm., thickness 1 cm.); the surface of the latter was yellowish-white, owing to the presence of an orange exudate, but, on scratching, it acquired the white appearance of starch. The starch was present as irregular grains of unequal size (10 to 30μ), as a rule bell-shaped on one side and cut off sharply on the other, but having occasionally three faces. They were frequently grouped in pairs, and in appearance closely resembled manioc starch, the hilum being indistinct, although a central star-shaped fissure was apparent in the burst grains. The starch was determined by extracting the pulverised sample with ether in a Soxhlet apparatus until all the colouring matter had been removed. The residue was then dried in air and hydrolysed with a preparation of pancreatic diastase (*cf.* Bourdouil, *Bull. Soc. Chim. Biol.*, **1931**, **13**, **809**). The large roots contained 41·4 per cent., and the discs 56·5 per cent. of anhydrous starch. The starch was extracted by shaking 50 g. of the powdered sample with 2 litres of water, and then separating the fibres from the starch on a No. 120 sieve with the aid of water. The starch, which settled rapidly and could be washed by decantation, was finally collected on cloth and dried in air (yield, 50 per cent. on the dry weight of the original material); it was then pale grey in colour. Attempts to extract and identify the colouring matter were unsuccessful. J. G.

Inorganic

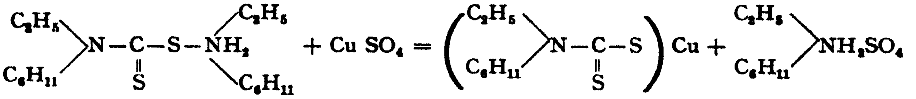
Analytical Applications of Dimine. M. Herrmann-Gurfinkel. (*Bull. Soc. Chim. Belg.*, **1939**, **48**, 94–103.)—The dithiocarbamate of cyclohexylethylamine, "dimine," used as a catalyst in the vulcanisation of rubber, is a crystalline substance, m.p. 93°, which volatilises with decomposition above 100° C.; solubility in water, about 5 g. per litre at 20° C. and 10 g. per litre at 80° C. It is decomposed, with evolution of carbon disulphide, by dilute mineral acids:



$$\begin{matrix}C_2H_5\\C_6H_{11}\end{matrix}\!\!>\!N-\underset{\overset{\|}{S}}{C}-S-NH_2\!\begin{matrix}C_2H_5\\C_6H_{11}\end{matrix} + 2HCl = CS_2 + 2\ \begin{matrix}C_2H_5\\C_6H_{11}\end{matrix}\!\!>\!NH_2\cdot Cl$$

With the salts of most metals, in neutral solution and in normal hydrochloric or sulphuric acid, dimine forms very bulky precipitates, the colours of which are as follows:—White: Pb, Hg^{II}, As^{III}, As^{V}, Sb^{III}, Sn^{II} (in neutral solution), Zn; Yellowish-white: Cd, Sb^{V}; Yellow: Ag, Bi (canary-yellow), Sn^{II} (in acid solution), Sn^{IV} (turning brown in air); Brown: Cu, Fe^{II} (greyish-brown), Fe^{III} (dark brown); Green: Ni (bright), Co (dark); Greyish-black: Hg^{I}. Manganous salts, which do not form precipitates in acid solution, give a brown one in neutral solution; molybdates in neutral solution give a yellow precipitate, which turns brownish-pink after addition of salts of zinc or tervalent bismuth and red after addition of hydrochloric or sulphuric acid or of aluminium salts; the uranyl ion, UO_2^{++}, forms a brick-red precipitate with dimine. Silver, lead, copper and zinc are also precipitated in *N* potassium hydroxide solution, and cadmium, nickel, cobalt and manganese in *N* ammonium hydroxide solution. The formation of a turbidity or colour with the reagent in very dilute solution is a very sensitive test for some metals. The limiting concentrations, in gram-atoms per litre, at which these were perceptible were approximately:—Colours: Cu $4{\cdot}10^{-6}$ (golden yellow); Fe$^{\text{III}}$ $2{\cdot}10^{-5}$, Bi$^{\text{III}}$ $4{\cdot}10^{-5}$, Ag $3{\cdot}10^{-4}$ (yellow); Mn $4{\cdot}10^{-5}$ (pink); Ni $4{\cdot}10^{-5}$ (greenish); Co $4{\cdot}10^{-5}$ (green); white turbidities: Sb$^{\text{III}}$ $3{\cdot}10^{-5}$, As$^{\text{III}}$ $3{\cdot}10^{-4}$, Cd $4{\cdot}10^{-4}$, Zn $4{\cdot}10^{-4}$. The test was made by adding 3 drops of a 0·5 per cent. dimine solution to 3 ml. of a dilute solution of the metallic chloride. Dimine is a much more sensitive reagent than hydrogen sulphide for the detection of copper, and traces of silver in solution can be detected by adding a few drops of dimine solution followed by a few drops of conc. ammonium persulphate solution; in presence of silver a blue colour, rapidly changing through green to yellow, is obtained.

Solutions of dimine can be standardised by titration with copper sulphate solution and can then be used for the determination of copper. A 0·8 to 0·9 per cent. dimine solution which has been prepared at 80° C. remains clear, when cold, for two or three days, and its strength, as determined by titration, does not alter for some weeks, in spite of the turbidity which forms through separation of the reagent in this supersaturated solution. The brown precipitate formed with copper sulphate solution coagulates and settles almost instantaneously, leaving the supernatant liquid clear, and the end-point of the reaction, when precipitation ceases, is clearly marked. The reaction is:



$$\begin{matrix}C_2H_5\\C_6H_{11}\end{matrix}\!\!>\!N-\underset{\underset{S}{\|}}{C}-S-NH_2\!<\!\begin{matrix}C_2H_5\\C_6H_{11}\end{matrix} + Cu\,SO_4 = \left(\begin{matrix}C_2H_5\\C_6H_{11}\end{matrix}\!\!>\!N-\underset{\underset{S}{\|}}{C}-S\right)Cu + \begin{matrix}C_2H_5\\C_6H_{11}\end{matrix}\!\!>\!NH_2SO_4$$

Copper may be also determined gravimetrically with dimine, the precipitate being dried, ignited and weighed as copper oxide. Test analyses with known weights, excess of dimine being used, gave percentage errors of +0·5, +0·1 and −0·5, respectively, the corresponding excess of dimine being 50, 10 and 10 per cent.

Iron has also been determined gravimetrically in test solutions of ferric chloride in which the iron, determined by the nitrite method, was equivalent to 0·0937 g. of Fe_2O_3 in 10 ml. Ten ml. of the solution were treated with 10 ml. of 10 per cent. ammonium chloride solution and, after dilution to 100 ml., with 140 to 190 ml. of a 0·8 per cent. solution of dimine, added, drop by drop, until an excess of 10 to 50 per cent. was present. The precipitate was filtered off, washed with about 400 ml. of 0·08 per cent. dimine solution, dried at 70° C., and ignited carefully until combustion of organic matter was complete. The residue was taken up with a few drops of nitric acid, the solution was evaporated, and the ferric oxide is re-ignited and weighed. In three out of four determinations results were 0·6 per cent. above theory.

Dimine may be used for the separation of iron from chromium without conversion of chromic salts into chromates. Chromium is precipitated by dimine only in very concentrated neutral solutions; this precipitation is prevented by the presence of ammonium chloride. Determinations, made by the method described, on 100-ml. samples containing 10 ml. of $M/10$ ferric chloride, 10 ml. of $M/10$ chromic chloride and 1 g. of ammonium chloride and variable amounts of hydrochloric acid show that the optimum concentration of acid for the analysis is $N/20$, but most of these results were slightly too high and there appears to be a constant source of error in the determination. For complete precipitation of the iron, excess of dimine sufficient to neutralise the acid present is required. The washing of the precipitate with 0·08 per cent. dimine is continued until all chlorides are removed; this requires approximately 500 ml. E. B. D.

Iodimetric Determination of Copper. S. K. Hagen. (*Z. anal. Chem.*, 1939, **117**, 26–30.)—The following process combines speed and economy while preventing the interference of nitrous compounds. A quantity of alloy containing about 0·2 g. of copper is dissolved in 10 ml. of nitric acid (1 : 4). The solution is boiled until the red fumes have been expelled, treated with 10 ml. of a solution containing 1·5 g. of lead nitrate, 100 g. of urea, and a little nitric acid per litre, stirred vigorously, and cooled to room temperature. After addition of 10 ml. of 10 per cent. potassium thiocyanate and 10 ml. of 1 per cent. potassium iodide solution, the solution is shaken and titrated at once with thiosulphate solution standardised against pure copper, starch being added towards the end. Addition of the lead salt is stated to produce an extremely sharp end-point. Any precipitate forming in the solution (urea nitrate) is disregarded. The interference of iron is overcome by adding sodium pyrophosphate before the thiocyanate. W. R. S.

Determination of Small Amounts of Nickel and Cobalt in Silicate Rocks. E. B. Sandell and R. W. Perlich. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 309–311.)—*Nickel.*—The method was designed for rocks containing about 0·01 per cent. of nickel, a content too low to be determined by the gravimetric method of Harwood and Theobald (ANALYST, 1933, **58**, 673). The rock sample (0·25 g.) is obtained in solution by acid attack or fusion as necessary, 5 ml. of 10 per cent. sodium citrate solution are added, and the solution is rendered slightly ammoniacal; 2 ml. of 1 per cent. alcoholic dimethylglyoxime solution are added, and the liquid is extracted with two or three portions of chloroform, with vigorous shaking each time for half-a-minute. The chloroform extract containing the nickel glyoxime complex is washed once by shaking with 10 ml. of dilute (1: 50) ammonia, and then shaken with two 4-ml. portions of 0·5 *N* hydrochloric acid. This decomposes the nickel glyoxime, and the nickel passes into the aqueous phase, in which it is determined by Rollet's method as follows:—The solution is diluted to 10 ml. with 0·5 *N* hydrochloric acid and 5 drops of saturated bromine water are added, followed by ammonia, drop by drop, until the bromine colour disappears, with 3 or 4 drops in excess; 0·5 ml. of 1 per cent. alcoholic dimethylglyoxime solution is added, and the colour developed compared in a Duboscq colorimeter with that formed by a standard nickel solution (less than 5γ per ml.) treated similarly, at the same time. Copper, cobalt, manganese, chromium and vanadium, in the amounts likely to be encountered in most igneous rocks, do not interfere; in test experiments, 100γ of cobalt gave a colour corresponding with 1·5γ of nickel; 100γ of copper treated gave no colour. It is stated that manganese in large quantities may cause trouble by oxidising nickel to the nickelic condition, in which it is not soluble in chloroform. *Cobalt.*—Extraction of the element with a carbon tetrachloride solution of dithizone from the ammoniacal citrate solution of the sample is employed. The carbon tetrachloride extract, which also contains the dithizonates of copper and other heavy metals, is evaporated to dryness, the residue is ignited to destroy organic matter, and the residual oxides are dissolved in *aqua regia*. The solution is treated with stannous chloride to reduce copper to the cuprous condition, and the cobalt is determined colorimetrically by the addition of ammonium thiocyanate and acetone, essentially as described by Tomula (*Z. anal. Chem.*, **1931**, **83**, 6); alternatively, it may be determined by the thiocyanate-amyl alcohol method (O. Hackl, *Chem.-Ztg.*, **1922**, **46**, 385). On a 1-g. sample of rock, as little as 0·0001 per cent. of cobalt may thus be determined.

S. G. C.

Separation of Cobalt from Manganese. J. G. Fairchild. (*Ind. Eng. Chem., Anal. Ed.*, **1939**, **11**, 326–327.)—Manganese phosphate is precipitated in ammoniacal citrate solution, cobalt remaining dissolved. The solution containing manganese and cobalt, to which 2 g. of citric acid per 125 ml. have been added, is treated by the Gibbs method for the precipitation of manganese (*cf.* Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929, p. 349). A small amount of cobalt tends to accompany the manganese in the precipitate, imparting a lilac colour. Re-precipitation of the manganese phosphate is advised. A simple method of correcting for co-precipitated cobalt is to determine it colorimetrically in the precipitate. The precipitate is dissolved in 20 ml. of dilute (1: 1) hydrochloric acid, a few crystals of sodium sulphite are added, and the solution is evaporated to 10 ml.; the cobalt chloride colour is matched colorimetrically against a series of standards containing known amounts of cobalt treated similarly. The cobalt contained in the filtrate from the manganese phosphate is precipitated as sulphide at *p*H 5·2; the sulphide precipitate is afterwards converted into sulphate in the ordinary way, and the cobalt is weighed as such. Good results were obtained in test experiments with 2 to 50 mg. of cobalt in presence of 100 to 250 mg. of manganese. Alkaline earth metals and magnesium are precipitated as phosphates with pronounced co-precipitation of cobalt and should therefore be absent.

S. G. C.

Colorimetric Determination of Iron in Glass with the Use of Thioglycollic Acid. R. C. Chirnside and C. F. Pritchard. (*Trans. Soc. Glass Tech.*, **1939**, **23**, 26–35.)—*Soda—Lime—Silica Glass.*—Ten ml. of hydrofluoric acid and 2 ml. of dilute (1: 6) sulphuric acid are added to a 0·2-g. sample of glass, contained in an iron-free platinum crucible. The liquid is evaporated to dryness, the residue is ignited and fused with 0·5 g. of sodium carbonate, the cooled mass is dissolved in 10 ml. of 1: 1 hydrochloric acid, and the solution is diluted to 100 ml. An aliquot portion is transferred to a 50-ml. Nessler tube, and 2 ml. of tartaric acid (10 per cent.), 2 ml. of dilute thioglycollic acid (1: 10) and 10 ml. of ammonia (1: 1) are added in that order. The purple-red colour of the iron-thioglycollic acid complex is matched against that of a similar solution (without sample), in another Nessler tube, titrated with standard iron solution (1 ml. = 0·00001 g. Fe_2O_3). A blank test on the reagents is advised. In absence of much alumina in the glass, fusion may be omitted: the solution in hydrofluoric-sulphuric acid is evaporated "to fumes," and the residue is dissolved, by heating, in water, with the addition of 5 ml. of conc. hydrochloric acid; the solution is diluted to 100 ml., and an aliquot portion is used for the colorimetric determination. *Alkali—Lead*

Oxide—Silica Glass.—A 0·2-g. sample is treated with mixed acids as before and evaporated "to fumes," 15 ml. of dilute sulphuric acid (1: 10) are added, the liquid is boiled, and the lead sulphate is allowed to settle out, filtered off and washed, and the iron determination is carried out on the filtrate. *Coloured Glass.*—Cobalt, which may be present, interferes with the iron determination by giving a dark yellow-green colour, and requires to be separated by zinc oxide treatment. After acid attack and fusion of the residue as described above, the fused mass is dissolved in 10 ml. of dilute hydrochloric acid (1: 1) and one drop of nitric acid is added to the hot solution to oxidise iron. The solution is diluted to 100 ml., and an aliquot part is neutralised with ammonia and just acidified with hydrochloric acid (pink colour with methyl red indicator); 100 mg. of pure zinc oxide are added, the liquid is well stirred and left for 10 minutes, and the precipitate is filtered off (No. 44 Whatman paper) and washed with water. The precipitate is dissolved from the paper with 10 ml. of warm dilute hydrochloric acid, the paper is washed, and iron is determined in the solution as previously described.

S. G. C.

Gravimetric Determination of Molybdenum as Trioxide. M. Straumanis and B. Ogrims. (*Z. anal. Chem.*, 1939, **117**, 30–47.)—The precipitation of molybdenum as sulphide (which is ignited to and weighed as trioxide) was re-investigated. The authors find that the formation of molybdenum blue is avoided by dilution of the solution to less than 0·03 g. of MoO_3 per 100 ml. Further, the solution must be free from strong oxidising agents and also from phosphoric or arsenic acid. The acid concentration (hydrochloric, sulphuric, or nitric) may vary between 0·02 and 0·1 *N*, precipitation in a pressure-flask being unnecessary. A maximum concentration of hydrogen sulphide should be aimed at; hence a rapid stream of the gas is passed into the cold solution for 5 to 10 minutes. While the gas is passing the liquid is boiled for 10 minutes, allowed to cool, set aside for an hour, and filtered. The dried precipitate is cautiously ignited over a Bunsen burner until the paper has charred, then heated for 15 minutes in an electric furnace the bottom of which is kept at 500° C., and weighed as MoO_3.

W. R. S.

Separation of Tantalum from Niobium. H. Wirtz. (*Z. anal. Chem.* 1939, **117**, 6–9.)—A combination method is briefly described in which the oxidimetric determination of niobium is carried out on a weighed tannin precipitate containing the whole of the tantalum with very little niobium. This mode of working reduces the error incurred in the volumetric determination of niobium (*cf.* ANALYST, 1924, **49**, 215) to an almost negligible amount.

The weighed mixed oxides, which may contain titania (the quantity of which can be determined colorimetrically), are fused with potassium bisulphate, the melt is dissolved in ammonium oxalate solution, and the solution (diluted to 400 ml.) is treated with a few drops of bromophenol blue indicator and 1 to 2 ml. of strong sulphuric acid. The boiling solution is carefully treated with ammonia (1 : 3) until the yellow tint of the solution changes to a distinct purple. After addition of 10 g. of ammonium chloride, 2 per cent. tannin solution is added (quantity not stated), which precipitates the whole of the tantalum and titanium with only

0·01 to 0·02 g. of niobic oxide. After 20 to 30 minutes' boiling the precipitate is collected under slight suction, washed with hot 2 per cent. ammonium chloride solution, and ignited to constant weight. The oxide is fused with bisulphate, and the melt is dissolved in succinic acid solution (Metzger and Taylor, *J. Soc. Chem. Ind.*, 1909, **28**, 818). A measured amount of titanic sulphate solution is added to prevent hydrolytic dissociation of the niobium compound during treatment in the Jones reductor (ANALYST, 1922, **47**, 534), and the reduced solution is caught in ferric sulphate solution. The lower end of the reductor is immersed in the ferric solution. (The Nb_2O_5 is reduced to Nb_2O_3.) The volume of 0·1 *N* permanganate solution required to reoxidise the added titanium salt is ascertained by a blank test, from the result of which the volume of permanganate solution consumed by the titania in the ignited tannin precipitate can be calculated. The total volume of permanganate solution equivalent to titania is subtracted from the volume used in the titration; the difference is calculated to niobic oxide. The tantalic oxide in the ignited tannin precipitate is computed by subtracting the sum of titanic and niobic oxides found by titration from the weight of the precipitate.

W. R. S.

Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Rhenium. H. H. Willard and G. M. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 305–306.)—To the hot solution (25 to 60 ml.) containing potassium perrhenate with sufficient sodium chloride to give a 0·5 *M* concentration in the final solution, a measured excess of tetraphenylarsonium chloride is added. The liquid is stirred and kept for several hours, preferably overnight. The white crystalline precipitate of tetraphenylarsonium perrhenate [$(C_6H_5)_4AsReO_4$] is filtered off on a Gooch crucible, washed with ice-cold water, dried at 110° C. and weighed. Alternatively to gravimetric determination, the excess reagent in the filtrate may be determined potentiometrically with iodine (*id.*, 1939, **11**, 186; Abst., ANALYST, 1939, **64**, 452). The solution may be neutral, ammoniacal or acid up to about 4 *N* strength of acid. Nitrate, bromide, iodide and fluoride should not be present in more than small amounts. Permanganate, perchlorate, periodate, thiocyanate, mercury, tin, vanadyl, bismuth, lead and silver ions interfere. Cadmium and zinc are not detrimental if the chloride concentration is low. Tungstate, molybdate and metavanadate ions do not interfere with the precipitation of perrhenate in ammoniacal or tartrate-containing solutions. S. G. C.

Determination of Nitrogen in the Complex Cyanides of the Heavy Metals. V. E. Tischenko and A. M. Samsonifa. (*J. Ob. Chem.*, 1939, **9**, 160.)—For the determination of nitrogen in complex cyanides the sample is heated with dilute sulphuric or hydrochloric acid in 100-ml. sealed tubes for 1 hour in a furnace at 270° C., 25 ml. of dilute acid (1 : 4) being used. The nitrogen is subsequently determined as ammonia by distillation from alkaline solution. With dilute sulphuric acid the error varied from —0·04 to —0·31 per cent. in determinations on the salts $K_3Fe(CN)_6$, $K_2Hg(CN)_4$, $KAg(CN)_2$, $K_4Co(CN)_6$, $K_2Ni(CN)_4$, from 0·0912 to 0·5700 g. of salt being taken. With dilute hydrochloric acid under identical conditions, the error was smaller, ranging from —0·02 to —0·09 per cent. for weights of salts from 0·3290 to 0·8200 g. E. B. D.

Determination of Nitrogen in Stainless Steels. T. R. Cunningham and H. L. Hamner. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 303–304.)—The method involves solution of the steel in acid and distillation of the ammonia; the recovery of nitrogen as ammonia from acid-insoluble nitrides of titanium, vanadium and tantalum is described. *Process.*—A 5-g. sample of the steel contained in a 300-ml. platinum dish with a well-fitting cover is dissolved as far as possible in 50 ml. of dilute (1 : 1) hydrochloric acid; 3 ml. of conc. hydrofluoric acid are added and the liquid is heated until all soluble material is dissolved [this treatment is not necessary if the sample dissolves completely in hydrochloric acid, and a platinum vessel is then not required]. The solution is transferred to a distilling apparatus, the distillation flask of which contains 500 ml. of water, 50 g. of sodium hydroxide, 20 g. of tartaric acid and some pieces of "spongy" zinc, the whole having been previously distilled for some time to remove possible traces of ammonia. The mixture is distilled, the distillate (200 ml.) being received in 0·02 *N* hydrochloric acid, and the excess of acid is back-titrated with standard alkali with the use of sodium alizarine sulphonate as indicator (end-point: disappearance of clear yellowish-green colour, or the first indication of brown); 1 ml. of 0·02 *N* acid ≡ 0·00028 g. of nitrogen. Any insoluble residue obtained in the acid attack of the steel, which may contain nitride of vanadium, titanium, tantalum, or niobium, is filtered off, and the nitrogen determination is carried out on the filtrate. The filter-paper and residue are digested by heating in a Kjeldahl flask with 20 ml. of conc. sulphuric acid, 10 g. of potassium sulphate, and 1 g. of copper sulphate; 15 to 30 minutes' heating is allowed after the liquid has become clear. The sulphuric acid liquid is then distilled with alkali as for the main steel solution, the combined result giving total nitrogen in the steel. A blank determination, and the use of ammonia-free distilled water, are advised. Results agreeing well with the vacuum-fusion method were obtained on 18 : 8 chromium-nickel steel containing tantalum, and a 24 per cent. chromium steel containing titanium.

S. G. C.

Detection of Nitrites in Presence of Nitrates. E. Percs. (*Magyar Gyogyszerest Tars. Ert.*, 1939, **14**, 30–31; *J. Pharm. Belg.*, 1939, **21**, 403.)—The solution under examination is neutralised and treated with 5 drops of sulphuric acid and 1 drop of trypan red (see *Colour Index*, No. 438); in presence of nitrites the orange-red colour gradually changes to bright violet, the reaction being complete in 10 minutes. The test will detect 0·005 mg. of nitrite, and by using 0·5 ml. of the solution in a porcelain dish the sensitivity may be increased to 0·001 mg.

D. G. H.

Microchemical

Hygroscopic Substances in Microanalysis. I. Drying and Weighing Solids. II. Drying and Weighing Liquids. H. K. Alber. (*Mikrochem.*, 1938, **25**, 47–56; 167–181.)—I.—Hayman's definition of degrees of hygroscopicity (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 256; 1938, **10**, 55) is adopted, and a procedure is described for use mainly with type B, in which a 5-mg. sample increases in weight by more than 25γ in 5 minutes on the balance; type C must be handled without coming into contact with the atmosphere, because even in a few seconds absorption of moisture would render the analytical results completely inaccurate. *Apparatus.*—A charging tube with ground cap is constructed from soft glass or Jena "Geräte glas," but it must not be of Pyrex, which tends to accumulate electrical charges. The tube, which is designed to hold 10 to 20 mg. of substance, weighs 1 to 5 g.; it is 2 cm. long and 0·5 cm. in diameter, and is provided with a long thin glass rod as a handle, 10 cm. long and 0·15 cm. in diameter, broadening to 0·3 cm. at the point of attachment to the base of the tube. The dead space in the ground-on cap should be as small as possible, and the joint, which must fit perfectly, should be 5 to 7 mm. in length. The tubes are supported in a small aluminium rack designed to fit in an Abderhalden drier, the cap of the charging tube being supported in the correct position for replacement, which is effected by pushing the handle of the tube. *Moisture determination.*—The charging tube is cleaned and dried for 15 minutes in the Abderhalden drier at the required temperature and pressure, dry air is then admitted, the drying agent ("anhydrone") is removed, and the cap is pressed into position with the aid of capillary forceps. The charging tube is left beside the balance for 20 minutes and then 5 minutes inside the balance with doors open and for 5 minutes with the doors closed. Shorter waiting periods are permissible when the drying temperature is below 100° C. A similar tube is used as a counterpoise and the weight is determined within 2γ. The sample is inserted by means of a 4-mm. spatula, and the tube is re-weighed after 10 minutes. The sample is then dried in the Abderhalden drier until constant weight is attained. Substances of types B and C may be successfully dried in this way; the method was tested with a large variety of substances, including nucleic acids, mercaptans, inorganic hydrates, etc. *Nitrogen (Dumas) determination on hygroscopic substances.*—The sample is dried in the charging tube, as described above, and transferred rapidly to a porcelain boat by opening the cap and tapping gently (a sufficient quantity of the sample for a duplicate analysis may be left in the tube—it does not absorb moisture when transference is rapid), and the tube is re-weighed. The sample in the boat is mixed with 40 to 80 mesh copper oxide in the combustion tube itself (see Milner and Sherman, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 427). *Carbon and hydrogen determination on hygroscopic substances.*—The sample is transferred from the charging tube to a platinum boat in a large desiccator containing P_2O_5, the cover is replaced on the desiccator and only removed while the boat is rapidly inserted into the side-arm combustion tube. The charging tube is capped and returned to the balance and re-weighed after about 15 minutes. This procedure is successful for type B compounds. For type C compounds the best method is to dry the sample in the combustion tube itself. When a number of analyses of one substance are required, satisfactory results may be obtained by making the determinations on undried samples and correcting for the moisture-content. The original sample is kept in closed charging tubes to prevent any change in moisture-content. It is assumed that the volatile matter is one substance only. When this is doubtful, a check analysis should be carried out on a dry sample.

II. Several procedures for drying hygroscopic liquids were tested; these vary according to the amount of sample available, contact with drying agent, complete separation of drying medium and liquid, and specific properties of the liquids, such as vapour pressure and viscosity. The following procedure is for the automatic filling of weighing capillaries with almost complete exclusion of atmospheric moisture: An ordinary Pregl weighing capillary is weighed and inverted over a micro-centrifuge cone containing the liquid sample and the drying medium, and is held in position by means of aluminium wire (0·5 mm. diameter) so that the capillary tip does not reach the drying agent. The centrifuge tube is placed in a side-arm test-tube fitted with a stop-cock through the stopper. The test-tube is evacuated, bubbles escaping from the weighing capillary; drying is continued and then dry air is admitted through the stop-cock, so that dry liquid automatically rises up the capillary. If the tip has been immersed suitably, an air-bubble follows the liquid and acts as a seal. The weighing capillary is then cleaned, sealed and re-weighed. In experimental tests on both the milligram and decigram scale, losses of material (due to various factors) were investigated and found to amount to 0 to 40 per cent., the greatest loss occurring with ethyl ether.

J. W. M.

2-4-Dinitro-α-naphthol (Martius yellow) as a Reagent for Thallium and Cobalt. A. Martini. (*Mikrochem.*, 1938, 25, 9–12.)—2-4-Dinitro-α-naphthol was tested as a reagent for alkaloids and for metals. Only amorphous precipitates are obtained with alkaloids and for the metals results were negative except with thallium and cobalt. The reagent is dissolved in pyridine and used when diluted with three volumes of water. A micro-drop (0·01 ml.) of a thallium nitrate solution (1 : 1000) is mixed on a slide with an equal-sized drop of reagent solution. Needle-shaped orange-yellow crystals form almost at once; *Limit of identification* 0·04γ, *concentration limit* 1:100,000. For the detection of such small amounts, it is advisable to evaporate the test solution to dryness before the addition of the reagent. Alternatively, the test may be applied to the detection of Martius yellow, a saturated solution of thallium nitrate being used as reagent. The test for cobalt is carried out by the same procedure as for thallium; *limit of identification* 0·5γ, *concentration limit* 1:10,000; an amorphous yellow precipitate is formed. Cobalt may be detected by this test in presence of 100 times the amount of nickel.

J. W. M.

Reviews

INDUSTRIAL CHEMISTRY. By WILLIAM THORNTON READ. Second Edition. Pp. ix + 605. New York: John Wiley & Sons, Inc.; London: Chapman & Hall. 1938. Price 25s. net.

In plan and arrangement this second edition closely resembles the original one, while the ground covered is also the same. The text, however, has been revised and brought up to date. The early chapters deal with general topics, such as the relation of chemistry to industry, the function of the chemist in industry, sources of information, economics, materials of construction, equipment and unit operations. These are written in an interesting manner and contain much useful information.

The remaining chapters deal with the manufacture of single products or groups of products, this grouping being based on chemical similarity, as may be seen from the following chapter headings: Sulphur and Sulphuric Acid; Fixed Nitrogen; Silicate Industries; Sodium, Calcium and Magnesium Compounds; Mixed Fertilisers; Hydrochloric Acid; Electrochemical Industries; Metallurgy; Petroleum; Animal and Vegetable Oils, Fats and Waxes; Carbohydrate Industries; Protein Industries; Rubber; Coal Products; Synthetic Drugs, Dyes and Resins; Explosives; Paints and Varnishes.

Such an arrangement leads to a certain amount of sectionalising of the information, so that, whilst the production of crude copper is dealt with in the chapter on metallurgy, the refining of the metal is placed in that on the electrochemical industries. Conversely, the fabrication of aluminium is described in the latter chapter, whilst its properties and alloys are listed in the former.

These chapters are, on the whole, well written and, although they do not pretend to deal exhaustively with each industry, they do cover a wide ground. Too wide, perhaps; for in certain places one gains the impression that in order to keep the size of the book within reasonable limits, the text has been rigidly condensed, with the result that occasionally it becomes vague or cryptic. Thus, in describing the Solvay process for the preparation of sodium carbonate, it is stated that ammoniacal brine is passed downwards through towers up which carbon dioxide is flowing, but no reason is given for the ensuing statement that the gas emerging from the top of these towers is mainly nitrogen. Again, in dealing with the recovery of iodine from Californian oil-well brines this sentence occurs: "the clarified brine is treated with just enough silver nitrate to precipitate the iodide as silver iodide from which it is liberated by steel scrap." As the text-book is intended mainly for the use of students, it would have been helpful if such statements had been amplified and more chemical equations provided.

The work is reasonably free from errors, except in the sections on synthetic drugs and dyes. Here they abound and are of a type one would hardly expect to find. Thus chloramine-T and dichloramine-T are stated to be ortho derivatives, while chlorazene (actually a synonym for chloramine-T) is given as the corresponding para compound. A number of the dyes listed have also been given incorrect, or, rather, incomplete graphic formulae, while acenaphthene and indanthrene are always referred to as acetnaphthene and inanthrene.

In spite of these blemishes the book contains much valuable information and provides a good one-volume survey of chemical industry. If it were equipped with references to original papers, articles or other text-books, it would be valuable to an even wider range of readers than students. G. R. DAVIES

MODERN CEREAL CHEMISTRY. Third Edition, Revised and Enlarged. By D. W. KENT-JONES. Pp. vii + 720. Liverpool: The Northern Publishing Co., Ltd. 1939. Price 30s.

The new edition of Modern Cereal Chemistry is approximately twice the size of its predecessor and contains four new chapters on:—Dough Testing Machines; Flour for purposes other than Breadmaking; Cereal and Balanced Rations for Livestock; The Microbiology of Cereals (A. J. Amos).

All the old chapters have been revised in the light of recent advances, not only in cereal chemistry, but also in other branches of science which affect the milling and baking industries. More than one hundred pages are now devoted to methods of analysis.

The results of most investigations into problems of cereal chemistry are described in detail, together with the author's own comments; the text—as in previous editions—is pleasingly full of references to cognate literature, and the book contains much useful information accumulated by the author during his years of wide experience in the milling industry. The chapter on moisture in wheat deals clearly and concisely with a subject which must have proved at some time or another a problem to many analysts.

The new chapters on dough-testing machines and the microbiology of cereals are very welcome, in that they provide, particularly on the subject of dough-testing machines, information not readily attainable in the literature.

Some points of criticism, however, must be raised on the chapter on "Cereal and Balanced Rations for Livestock." In this chapter some of the definitions of feeding stuffs are misleading. Maize gluten feed, for instance, is prepared from maize in the production of maize starch and not, as stated in the text, in the manufacture of molasses.

In the section on oil-cakes it should be more clearly indicated that such cakes should be free from contamination with the poisonous castor-oil seed. The limit of castor-oil seed content as indicated by 0·005 per cent. of castor-oil seed husk, as given in the text, is sometimes fixed in commercial contracts as a limit beyond which the purchaser of a cargo or parcel may be entitled to claim "total rejection"; but the danger of this contamination is further recognised in such contracts by the infliction, on the vendor, of a money penalty per ton on a sliding scale for the presence of lesser quantities of castor husk down to even 0·001 per cent.

In connection with the author's reference to hydrocyanic acid and linseed cake, it is not made clear that the function of boiling water, which is very properly emphasised in the preparation of linseed gruel for calves, is not to expel hydrocyanic acid, but to kill or cripple the enzyme which may liberate it from the glycoside normally present.

The expression "Oat Meal" is used by the author to indicate ground oats. Ground oats are usually commercially described as such, not as "Oat Meal."

Oat Meal is meal made from de-husked oats, as for human consumption. It is true that ground barley is always called "Barley Meal," but the analogous expression "Oat Meal" is not used for ground oats.

These minor criticisms, however, apply only to a portion of the book which may be regarded as supplementary to its main contents, for the re-issue and expansion of which the author deserves warm gratitude. J. HUBERT HAMENCE

A TEXTBOOK OF PHARMACOGNOSY. By T. C. DENSTON, B.Pharm., A.I.C., Ph.C. Third Edition. Pp. xvi + 582. London: Sir Isaac Pitman & Sons, Ltd. 1939. Price 20s. net.

The publication of a third edition of a textbook on any subject is testimony that it meets the requirements of a number of purchasers, but it also gives the author an opportunity to extend, amplify, and improve the original copy. In this instance, the third edition has permitted a large amount of revision, and the inclusion of many fresh chapters, which indicate the increasing scope of the subject.

Materia Medica has always been correlated with botany because so many of the substances employed in medicine are of vegetable origin, but it is only during recent years that *pharmacognosy* has attained a definite place in a university syllabus. The modern textbook deals with something more than the botanical name, habitat and chief constituents of the important drugs, and some of the sections in this book possess a very definite educational value.

A chapter on drug constituents and their applications in pharmaceutics, contains, in the space of some sixty pages, the real essentials of pharmacognosy, and the section dealing with vitamins is as comprehensive as any short account of these relatively new substances can be while new facts are constantly being added to our present knowledge.

The section dealing with the cultivation, collection, stabilisation and preservation of drugs will be of service to students and others approaching the subject with an open mind. Such information can only be obtained by practical experience, and it has been very comprehensively dealt with in the space available.

The chapters devoted to the description of leaves, flowers, seeds, fruits, plants and herbs, barks, roots and rhizomes, are framed in the manner usual for a textbook on materia medica, and are fully illustrated and complete in detail, although some of the drawings leave out certain undefinable characteristics which only practical handling of the particular drugs can impart to a buyer or student. A photographic illustration of digitalis on page 119 affords a perfect picture of all the details by which the plant can be identified, but the drawing on page 124, and those on 127, would be of no practical assistance to a novice hoping to identify any adulterants. This lack of detail in the sketches is more apparent in the representations of rhubarb, jalap, and ipecacuanha, and suggests that the artist should pay a visit to the drug warehouses of the Port of London Authority to seek the familiarity which only comes when handling drugs in bulk. In contrast to these, the drawings on figures 85 and 86 depict what are typical structures in such a way as to make them recognisable when found under a microscope.

The sections dealing with oils, fats, and waxes, and those on volatile oils, are comprehensive, and include the official tests of the British Pharmacopoeia and some useful illustrations. A novel section consists of a series of maps showing some of the geographical features of parts of the world too well-known to need depicting, but a list of drugs and the countries where they are produced may be of service to those needing such information.

This is essentially a book for students, but the information is reliable and well arranged, and the recent additions and improvements will make it a useful book of reference. The line-drawing illustrations are contributed by Mr. M. Riley, and the new plates dealing with fibres, plant hairs and insect pests are from the hands of Miss Rosemary Butterfield, B.Pharm. C. EDWARD SAGE

THE CHEMISTRY OF MILK. By W. L. DAVIES, Ph.D., D.Sc., F.I.C. Second Edition. Pp. xiv + 534. London: Chapman & Hall. 1939. Price 25s.

That a second edition of this book has been called for is proof that it fills a useful position in the library of the dairy chemist. The revision has been, on the whole, well and carefully done, though there are a few typographical errors.

Some subjects are treated in greater detail than is necessary in a book which is not a practical treatise; for example, the preparation of pure casein (p. 146) and the description of the Kay phosphatase test (p. 363). On the other hand, there are certain curious omissions; for instance, there is no reference to the Lampitt and Hughes method for the accurate determination of the solubility of milk powders, which is still the best that has been published, nor to those useful weapons in the investigation of fat oxidation, the peroxide and Kreis tests; while the important effect of dilution on the titratable "acidity" of milk is mentioned, the equally important effect of the amount of indicator (to which attention was directed by Pizer) has not been mentioned. Dr. Davies has done a distinct service in directing attention to the relative inaccuracy of the figures for total solids based on lactometer readings; it would, however, be interesting to learn his authority for the statement that differences of +0·5 to —0·4 are possible. In the paper by Bartlett, Golding and Wagstaff referred to, the maximum error from actual determinations is shown to be about +0·28 to —0·10—figures that agree closely with those obtained in the writer's laboratory after allowance had been made for errors due to the physical condition of the fat, and in reading the lactometer and Gerber tubes; there is also considerable doubt whether at any time there is a significant change in the specific gravity of the solids-not-fat.

The author is less happy on the technological than the scientific side, which is to be expected, as years of experience are the only method of obtaining competence in any branch of the subject. It is not intended, however, to dissect the book paragraph by paragraph, but it is desirable to correct the statement on p. 428, referring to atmospheric roller-dried powder, that "when the product is intended for human consumption," "this process is disadvantageous," because of its lower solubility. This is not borne out by the fact that practically all maternity centres use these powders for infant feeding.

Despite these criticisms the book is a useful compilation "full of meat," and the tables have proved particularly valuable. If any student requires subjects for research in dairy chemistry, he has only to note how frequently subjects with the words "may be," "possibly," and "probably" occur. E. B. ANDERSON

WOOD PULP. By JULIUS GRANT, Ph.D., F.I.C. Pp. xi + 209. Leiden: Chronica Botanica Co.; London: Wm. Dawson & Sons, Ltd. 1938. Price 7 guilders (about 16s.).

This volume, of some 200 pages, is one of a new series of plant science books published in English by Chronica Botanica of Leiden, Holland. The author, whose experience in paper-making and allied subjects is well-known, states in his preface that while the series of publications is intended to cater especially for those interested in plant science, "it has been felt that wood pulp and the uses to which it is put has now become of such widespread interest and importance, that the opportunity should be taken to produce a work which will also appeal to students of other sciences as well as to general readers." In the present volume the author has definitely fulfilled this object.

The book gives a complete account of wood pulp in 20 short chapters, each one of which deals briefly and clearly with some necessary aspect of the subject. The first four chapters will be of particular interest to the botanist as well as to the general reader. They deal with the nature of pulp, the structure and growth of wood, and the distribution of wood pulp forests. A very interesting chapter on the historical development of the art of paper-making and the use of wood pulp—a subject the author has made particularly his own—follows. The structure of cellulose and wood fibres and the identification of the different types of wood used in pulping are then discussed.

The more technical side—the preparation of the wood, the sulphite, soda, and sulphate processes—is next considered, and here the simple chemistry, for example, of the sulphate process, is fully explained, so that the reader with little chemistry can follow the various stages. A sufficient account of the working of each process is given.

Bleaching is then discussed, and the modern use of chlorine to remove lignin prior to treatment with hypochlorite is explained. The mechanical purification of pulp and the utilisation of by-products are included, and final chapters deal with testing by physical and chemical means, and valuation of the pulps produced. The analytical processes given are, in many instances, those specified by The Technical Association of the Pulp and Paper Makers' Association of America. A few typical analyses would have helped the general reader of this section.

The uses of pulp for paper, rayon and many other purposes are fully described, and a few words as to paper and wood pulp in the future conclude the volume, which can be recommended as a well-written and most interesting treatment of the subject. C. DORÉE

HAIR-DYES AND HAIR-DYEING CHEMISTRY AND TECHNIQUE. By H. STANLEY REDGROVE, B.Sc., F.I.C., and J. BARI-WOOLLSS. Pp. 214. London: William Heinemann, Ltd. 1939. Price 10s. 6d.

This is the third edition of "*Blonde or Brunette?*" first published by Redgrove and (the late) G. Foan in 1929, and, like the original edition, has two distinctive merits: one that it is a collaboration between a skilled chemist and a practical hairdresser, and the other that it is the only book in our language dealing comprehensively with this subject. Both the artist and the chemist may be included in the quotation from Thomas Moore:

> While some bring leaves of henna, to imbue
> The fingers' ends with a bright roseate hue,
>
> And others mix the Kohol's jetty dye
> To give that long, dark languish to the eye.

The artist, in the shape of the practical hairdresser, has reigned in this field since the days of Enoch, and it is only of late years, with the advent of the new types of dye, that the subject has begun to receive from chemists the attention it deserves. The manufacture of hair-dyes and the technique of hair-dyeing are now quite an important branch of industry, and we are indebted to the authors for collecting and sifting so much information; they have given a connected scientific exposition of the subject in simple language.

After a general survey of the structure and properties of hair there follow chapters on bleaches (of which there are many), kohl, lead and silver dyes, tannin rasticks, walnut, henna, rengs, chamomile, and the wide field of the diamine class. The chemistry of each is explained, and practical applications are outlined. Then follow some ten chapters on the practical technique of hair-dyeing, and finally a section on grey hair and a bibliography.

Chemists will, of course, be mainly interested in Mr. Redgrove's part, which deals with the composition of various hair-dyes and mixtures. This section is excellent, the information is up-to-date and, so far as the reviewer can test it, accurate. It is, of course, inevitable that *p*-phenylenediamine should be discussed at some length; it is indeed a versatile compound, and if it does cause dermatitis sometimes to the few, it brings brightness to the million by the variety of shades that it can be induced to afford. Many are the ingenious devices which have been put forward to remove its irritant properties, but they are at best only partly effective; yet this substance remains the best all-round hair-dye. Its reactions and oxidation products in the presence of poly-phenols still offer an almost unexplored field for research.

The book as a whole is well written and very informative; it is likely to be most useful to all of us who have occasion to analyse hair-dyes or similar products and is full of interest, too, to the general reader. We warmly commend it.

H. E. Cox

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Death

WITH deep regret we record the death of Mr. H. T. Lea, formerly Secretary of the North of England Section. An obituary notice will be published later.

Obituary

HENRY FRANCIS EVERARD HULTON

HENRY F. E. HULTON was the son of Everard Hulton, Mus.Bac., and was born at West Brompton, London, on August 13th, 1874.

He received a private education, and then entered the City of London School in 1891, two years later becoming a pupil at Finsbury Technical College and remaining there for three years. On leaving he obtained a post with Messrs. Morris and Moritz, the well-known brewing consultants, and while there passed the Inter. B.Sc. examination. From 1903 to 1905 he was chemist at Messrs. Taylor's maltings at Sawbridgeworth, and during this period was an avid reader of the works of the Latin poets and of Tennyson, Huxley and H. G. Wells, retaining these interests throughout his life. Following this, he joined the scientific staff of Messrs. Watney Combe Reid & Co.'s brewery at Pimlico under Mr. J. L. Baker, and retained this post until his death. He attained the F.I.C. qualification in 1916, was an abstractor for THE ANALYST during a period of ten years, and subsequently served on the Publication Committee and on the Council of this Society.

In early manhood his chief recreation was cycling, both in this country and on the Continent, this being replaced later by pictorial photography, and subsequently by a life-long interest in botanical and geological rambles, for nothing gave him greater pleasure than the discovery of an unknown wild or garden plant and carrying out the often tedious process of identification. The "messiness" of zoology was repellent to his nature, and his interest in animal life in general was but slight.

During the last thirty-four years his days were devoted to the varied work of a brewing laboratory, and in conjunction with J. L. Baker he carried out extensive researches upon the action of diastase on starch in connection with the chief reaction occurring in the mash tun. These investigations culminated in a series of joint papers published mainly in the journals of the Institute of Brewing and the Chemical Society.

Hulton was an able and versatile chemist, severely critical of results, having a logical mind and a quickness of perception which at times was somewhat embarrassing to those with this faculty less developed. He had little ambition, but was methodical and painstaking and contented to carry out his duties in the best possible manner. With the true spirit of the man of science he entered occasionally into the menial work of the laboratory with the same enthusiasm that he displayed in carrying out a complex analysis.

He possessed a wide outlook on life and a great interest in music and art; the charm of manner and keen, kindly humour with which he was endowed, together with an entire absence of pretension, rendered him an admirable companion and a delightful conversationalist. In some ways he exhibited curious contrasts, for at times he alternated between shrewdness and simplicity, impulsiveness and caution, neatness and extreme untidiness. Whilst held in great respect by a wide circle of friends and colleagues, his modesty rendered him entirely oblivious to their high opinions, and occasionally he somewhat sadly deplored the supposed fact that he was friendless.

During the last few years it was evident to those in close association with him that his health was slowly declining, but his death, which occurred in a London nursing home on April 26th, 1939, was totally unexpected.

He was twice married, first to Miss B. H. Clift, and, after her death, to Miss Edwina M. Costin, who survives him, but he left no family.

His passing has deprived his colleagues of a loyal and sincere friend, whose genial presence and upright character will not readily be forgotten.

T. J. WARD

A Method for the Approximate Determination of some of the Unsaturated Minor Component Acids of Pig and Other Fats

BY T. P. HILDITCH, D.SC., F.I.C., AND W. H. PEDELTY, M.SC., A.I.C.

(*Read at the Meeting of the North of England Section, January 28, 1939*)

IN the course of investigations undertaken on behalf of the Department of Scientific and Industrial Research (Food Investigation Board) on the composition of a large number of pig depot and perinephric fats, it was desired to make comparatively rapid determinations of certain of the component acids, especially the more unsaturated minor components, linoleic acid and highly unsaturated acids of the C_{20} (and C_{22}) series. In certain respects, notably in connection with softness or with development of rancidity, the comparatively small amounts of these acids may play a more important part than the much larger proportions of oleic acid which are always present.

Iodine values and saponification values of the whole fats are of little value as a guide to the varying proportions of the different unsaturated acids which are present in different pig (or similar) fats. The additional determination of thiocyanogen values is, again, insufficient to lead to determinations of both the linoleic acid and the highly unsaturated C_{20} and C_{22} acids.

The whole of the component fatty acids of fats of this type can be quantitatively determined with considerable accuracy by the "ester-fractionation" method, in which the total mixed fatty acids are first divided into "solid" and "liquid" acids by separation of their lead salts from alcohol, followed by conversion of each group of acids into the corresponding methyl esters, and fractional distillation of these at low pressure (0·2 mm.). Complete analysis of a fat by the ester-fractionation method usually takes 17 to 20 days, requires 100 to 200 g. of fat and involves lengthy calculations; it is therefore not suitable for adoption as a routine method for small but numerous samples of fat.

The present communication deals with attempts to devise a more rapid, yet reasonably reliable, method for determining the proportions of the major and the more important unsaturated minor component acids of fats such as lard, etc. (In such rapid methods as those about to be described it is not possible to take account of minor components such as myristic and tetra- and hexa-decenoic acids; since, however, the sum of these never exceeds about 4 per cent. of the total fatty acids and, more important, since their proportions in pig fats are nearly constant and are largely independent of dietary conditions, it is usually unnecessary to know their specific proportions.)

Four shortened methods have been devised and tested on sixteen specimens of pig fats, the component acids in which had been determined by the full ester-fractionation procedure. Of these, three were found either to be unduly lengthy or to give results which did not accord very well with the ester-fractionation data; these are only discussed briefly here. The remaining method, which gave the most consistent results and was also, fortunately, the shortest and simplest in execution, is given in full detail.

The three, less satisfactory, methods mentioned were briefly as follows:

(1) Mixed fatty acids from the saponified fat (50 g.) were crystallised, as lithium salts, (i) from acetone,[1] and (ii) the acetone-insoluble lithium salts from 80 per cent. alcohol[2]; the alcohol-insoluble lithium salts from the latter crystallisation were converted into acids and then into lead salts, which were separated according to their solubility in alcohol. The four groups of acids so obtained were examined for mean equivalent and iodine value, and those from the acetone-soluble soaps for the amount of ether-insoluble polybromo-additive compounds produced on treatment with bromine. The results showed good agreement with the ester-fractionation data, but the method was rejected as being too lengthy and cumbersome.

(2) The fat (50 g.) was first separated by crystallisation from acetone into three fractions of increasing solubility.[3] The saponification equivalent and iodine

value of each fraction, and the thiocyanogen values of the two most soluble fractions, were determined; the acids from the most soluble fraction were submitted to the lithium salt-acetone separation, and those from the acetone-soluble lithium salts were brominated. This procedure did not give such accurate or reproducible figures as method (1), and was also rather lengthy.

(3) The saponification equivalent and iodine and thiocyanogen values of the original fat were determined, whilst a portion (25 g.) was converted into fatty acids, and the portion of the latter yielding acetone-soluble lithium soaps was separated and brominated in ether. This procedure is shorter than methods (1) and (2), but did not always give results according with those obtained by ester-fractionation.

The method finally found most satisfactory was the following:

(4) The mixed fatty acids from the fat (about 30 g.) are separated as lithium salts from acetone. The yield of ether-insoluble bromo-additive products from the acids from the acetone-soluble lithium salts is determined, and from this the percentage of C_{20-22} acids is obtained as described later (*cf.* p. 643). The iodine and thiocyanogen values of the acids from the acetone-insoluble lithium salts are determined, and from the results the total saturated, oleic and linoleic acid contents are found. This, of course, presupposes (i) that no linoleic acid is left in the form of acetone-soluble lithium salts and (ii) that all the highly-unsaturated C_{20-22} acids remain in solution in acetone as soluble lithium salts. Neither assumption is likely to be wholly correct but, since the final results obtained are in fair accordance with those determined by ester-fractionation, it would appear that the errors introduced by these assumptions cancel out. The method is relatively rapid and, in view of the accordance with the data from ester-fractionation shown in the sixteen pig fats examined (*cf.* Table III, p. 645), it is recommended as a considerable improvement on the simple determination of iodine and thiocyanogen values alone as a guide to the important unsaturated minor components (linoleic and highly-unsaturated C_{20-22} acids) present in these fats.

DETAILS OF THE RECOMMENDED METHOD.—The fat (about 30 g.) is refluxed with 100 ml. of 10 per cent. alcoholic potash for three hours, the alcohol is removed and the fatty acids are liberated with sulphuric acid and extracted with ether (200–300 ml.). The ethereal extract is washed with water until the aqueous washings are neutral to Congo Red paper, and then placed in a weighed 500-ml. round-bottomed flask, and the ether is removed by distillation, after which the flask and its contents are heated at 100° C. in the vacuum of a water-pump until all moisture has been removed. The weight of fatty acids obtained is noted.

Lithium soap separation from acetone.—Saturated lithium hydroxide solution (approx. 4 *N*, *i.e.* 96 g. per litre, at ordinary temperature) is conveniently prepared by dissolving the fresh hydroxide in boiling distilled water until the latter is saturated, cooling somewhat, and filtering the warm solution through glass-wool. The solution should be stored in well-stoppered bottles to exclude atmospheric carbon dioxide.

The mixed fatty acids (about 25 g., weighed to 0·01 g.) are dissolved in 95 ml. of pure acetone, to which 5 ml. of an acetone solution of phenolphthalein (0·4 per cent.) are added, and the hot acetone solution is titrated with saturated lithium hydroxide solution until alkalinity is reached. (Vigorous shaking is necessary during the titration in order to break up any lumps of separated soap which may be produced; titration to the nearest 0·5 ml. of lithium hydroxide solution is sufficient.)

The solution is then adjusted so that the solvent consists of 95 per cent. acetone,* boiled under reflux for a few minutes, and set aside to cool for two hours at room temperature. The insoluble soaps are removed by filtration on a Buchner funnel and then washed with a small quantity (one-tenth of total volume of solution) of 95 per cent. acetone. The filtrate, containing the soluble lithium soaps, is completely transferred to a separating funnel, decomposed by the addition of an excess of dilute hydrochloric acid and then extracted twice with ether. The ethereal solution is washed free from mineral acid, the solvent is removed, and the fatty acids are dried *in vacuo* at 100° C. and weighed. The insoluble lithium soaps are transferred back to the flask, and decomposed by warming with dilute hydrochloric acid; the filter-funnel is alternately washed with hot dilute hydrochloric acid and ether in order to recover all traces of fatty acids. These washings and the main bulk of the decomposed soaps are completely transferred to a separating funnel and, after two extractions with ether, the fatty acids are isolated as previously described.

The whole of the lithium soap-acetone procedure should be quantitative within experimental error and, starting with 25 g. of fatty acids, an aggregate recovery of 25 ± 0·1 g. is satisfactory. The sum of the two fractions of acids (not the initial weight of acids taken) is used for expressing each fraction as a percentage of total fatty acids.

The iodine and thiocyanogen values of the acids from the insoluble lithium soaps are then determined.

Bromination of acids from soluble lithium soaps.—This fraction of fatty acids comprises 3·5 to 4·5 per cent. of the total used in the separation. The acids are accurately weighed, 10 volumes of ice-cold dry ether (sp.gr. 0·720) are added and, with the flask cooled in an ice-salt freezing-mixture, bromine is added, drop by drop, until a bright red colour indicates excess of halogen. At this point the flask is removed from the freezing mixture and kept at 0° C. overnight in a refrigerator. The precipitate of insoluble polybromo-additive products is filtered on a clean, dry and weighed sintered glass crucible, washed with small quantities of ice-cold ether to remove excess of bromine and soluble bromo-acids, dried at 80° C. in an electric oven, and finally dried in a vacuum desiccator to constant weight. The yield of polybromo-additive products is expressed as a percentage of the original weight of fatty acids taken for bromination and this figure is referred to as "per cent. of polybromides."

Calculation of percentage of highly-unsaturated C_{20-22} *acids from "per cent. of polybromides."*—It is well known that the yield of insoluble polybromo-additive products obtained from polyethenoid acids does not give the full measure of the latter. For the present purpose an arbitrary method of calculation has been employed, based upon the corresponding data for yield of polybromides obtained from the residual ester fractions, rich in esters of unsaturated C_{20} and C_{22} acids, obtained in the ester-fractionation analyses of the sixteen pig fats. In the ester-fractionation analyses, after removal of unsaponifiable matter from these residual fractions, the saponification equivalents are determined and the amount of C_{20-22} acids calculated therefrom, the constituents being unsaturated C_{18} acids of known equivalent and the C_{20-22} acids (taken at an average equivalent of 316). Portions of the fatty acids from these residual fractions were also submitted to the bromination procedure described above, and the "per cent. of polybromides" recorded in each instance. The "per cent. of polybromides," when plotted against the known percentage of C_{20-22} acids in the corresponding residual ester-fraction, formed an approximately linear graph over the range involved in our determinations, and the calculated amounts of C_{20-22} acids corresponding to the "per cent. of polybromides" obtained from the acids from the acetone-soluble lithium salts were deduced from this relationship.

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* The total volume of the solution being 20 times the volume of water added in the titration, and the latter being approximately 10/11 × ml. of lithium hydroxide solution used, the adjustment to 95 per cent. acetone is made by the addition of [(19 × 10/11 × ml. of lithium hydroxide solution used) − 100] ml. of pure acetone.

The data from which these relations were derived (*in italics*) and the derived data for 5 per cent. increments in yield of "polybromides," are shown in Table I.

TABLE I

ESTIMATION OF PER CENT. OF C_{20-22} ACIDS FROM PERCENTAGE YIELD OF POLYBROMIDES

Polybromides Per Cent.	C_{20-22} acids Per Cent.
8·2	*30·8*
10	34·0
15	42·5
20	51·0
21·7	*56·5*
25	59·5
30	68·0
32·7	*76·5*
33·0	*69·3*
33·5	*69·0*
35	76·5
40	85·0
45	93·5
46·0	*95·0*

ANALYSES OF SIXTEEN PIG FATS BY THE RECOMMENDED METHOD.—The data obtained during the examination of sixteen different pig fats by the procedure described above are collected in Tables II and III. Table II gives analytical details of the acids obtained in each case from the acetone-insoluble and acetone-soluble fractions of the lithium soaps of the mixed fatty acids, whilst Table III shows the composition of the acids ("S") deduced from the data in Table II, together with the corresponding results ("E"), for each fat, as determined by the ester-fractionation method.

TABLE II

ANALYTICAL DATA OBTAINED BY THE RECOMMENDED METHOD

Pig. No.	Acids from insoluble lithium salts				Acids from soluble lithium salts		
	g.	Per Cent.	Iodine value	Thio-cyanogen value	g.	Per Cent.	"Poly-bromides" Per Cent.
72 (O)	26·56	95·8	59·6	53·2	1·16	4·2	31·6
74 (O)	27·59	95·6	57·0	49·3	1·25	4·4	17·4
74 (I)	28·21	96·5	51·1	44·8	1·01	3·5	31·6
73 (O)	25·54	96·0	55·6	49·7	1·06	4·0	27·0
73 (F)	24·38	96·2	47·8	43·5	0·96	3·8	35·0
82 (O)	27·38	95·9	61·1	52·4	1·17	4·1	45·0
167 (O)	25·28	96·7	62·5	51·9	0·86	3·3	36·1
167 (I)	28·99	96·4	57·2	48·8	1·10	3·6	43·7
167 (F)	26·98	96·4	52·5	44·0	1·00	3·6	43·2
173 (O)	25·22	96·4	55·7	46·0	0·93	3·6	30·2
173 (I)	28·36	96·2	50·7	41·8	1·13	3·8	51·0
173 (F)	30·27	94·8	48·9	39·8	1·66	5·2	30·7
138 (O+I)	26·25	96·4	54·7	48·1	0·96	3·6	35·3
175 (O)	25·86	95·8	60·1	51·6	1·12	4·2	45·3
175 (I)	28·49	95·9	56·0	48·2	1·23	4·1	43·3
175 (F)	28·94	96·3	52·7	44·5	1·10	3·7	46·1
175 (F) (duplicate)	26·32	96·0	52·6	44·7	1·10	4·0	42·9

(O) = outer layer of back fat; (I) = inner layer of back fat; (F) = flare (perinephric) fat.

TABLE III

COMPONENT FATTY ACIDS (PER CENT. WT.) OF SIXTEEN PIG-FATS

"S": From the data in Table II.

"E": Determined by the full ester-fractionation procedure.

Fat No.:	72 (O)		74 (O)		74 (I)	
Acids	"S"	"E"	"S"	"E"	"S"	
Total saturated	39·2	39·1	43·2	41·5	48·4	47·3
Tetradecenoic	—	0·1	—	0·2	—	0·3
Hexadecenoic	—	2·0	—	2·7	—	2·7
Oleic	49·8	51·0	44·3	47·5	41·3	40·9
Linoleic	6·8	5·3	8·1	6·0	6·8	7·1
Unsaturated C_{20-22}	3·0	2·5	2·1	2·1	2·5	1·7
Undetermined	1·2	—	2·3	—	1·0	—

Fat No.:	73 (O)		73 (F)		82 (O)	
Acids	"S"	"E"	"S"	"E"	"S"	"E"
Total saturated	42·7	42·8	49·7	49·4	40·1	38·9
Tetradecenoic	—	0·2	—	0·1	—	0·2
Hexadecenoic	—	2·4	—	1·5	—	2·0
Oleic	46·8	47·0	41·9	41·2	46·6	48·1
Linoleic	6·2	5·2	4·6	5·7	9·2	7·8
Unsaturated C_{20-22}	2·6	2·4	2·9	2·1	3·9	3·0
Undetermined	1·4	—	0·9	—	0·2	—

TABLE III—*continued*

Fat No.:	167 (O)		167 (I)		167 (F)	
Acids	"S"	"E"	"S"	"E"	"S"	"E"
Total saturated ..	41·0	39·9	44·2	45·0	49·4	49·8
Tetradecenoic ..	—	0·2	—	0·2	—	0·1
Hexadecenoic ..	—	1·7	—	2·4	—	1·0
Oleic	44·4	45·6	43·3	40·0	38·0	38·8
Linoleic	11·3	9·1	8·9	9·6	9·0	8·3
Unsaturated C_{20-22} ..	2·6	3·5	3·3	2·8	3·2	2·0
Undetermined ..	0·7	—	0·3	—	0·4	—

Fat No.:	173 (O)		173 (I)		173 (F)	
Acids	"S"	"E"	"S"	"E"	"S"	"E"
Total saturated ..	47·3	46·1	51·6	50·5	52·9	52·7
Tetradecenoic ..	—	0·2	—	0·2	—	0·2
Hexadecenoic ..	—	2·6	—	1·7	—	2·2
Oleic	39·0	39·5	35·2	37·2	32·4	34·1
Linoleic	10·3	8·2	9·4	7·1	9·5	7·3
Unsaturated C_{20-22} ..	2·4	3·4	3·8	3·3	3·6	3·5
Undetermined ..	1·2	—	—	—	1·6	—

Fat. No.:	138 (O+I)		175 (O)		175 (I)	
Acids	"S"	"E"	"S"	"E"	"S"	
Total saturated ..	45·0	43·5	40·9	40·3	44·6	43·5
Tetradecenoic ..	—	0·2	—	0·2	—	0·2
Hexadecenoic ..	—	3·5	—	1·9	—	1·7
Oleic	44·4	47·8	45·9	46·8	43·1	44·2
Linoleic	7·0	3·1	9·0	7·9	8·2	7·3
Unsaturated C_{20-22} ..	2·8	1·9	3·9	2·9	3·7	3·1
Undetermined ..	0·8	—	0·3	—	0·4	—

Fat. No.:	175 (F)		
Acids	"S"	"S"	
Total saturated ..	48·7	48·4	47·6
Tetradecenoic ..	—	—	0·3
Hexadecenoic ..	—	—	1·8
Oleic	38·9	39·2	40·3
Linoleic	8·7	8·4	8·1
Unsaturated C_{20-22} ..	3·5	3·6	1·9
Undetermined ..	0·2	0·4	—

The agreement between the results by the two methods is, it is felt, sufficiently close to justify the use of the shortened method as one which is more rapid than the full ester-fractionation process, which avoids any distillations of esters or acids, and which gives much more complete information as to the minor unsaturated acids present than can be obtained by analytical characteristics applied to the whole fats. It is true that the method requires between two and three days to complete the analysis of any one specimen of fat. A large proportion of this time, however, is represented by the two crystallisations which have to remain at 0° C., respectively, for two and for sixteen hours (overnight). The actual time in which the attention of the analyst is required is thus considerably less, and, of course, any convenient number of fats can be dealt with concurrently.

It may be noted that the saturated acids are returned collectively, and not individually. Attempts to determine the proportions of palmitic and stearic acids, by employing the saponification values of the acids from the acetone-insoluble lithium salts in conjunction with their iodine and thiocyanogen values, have not led to satisfactory concordance with the data from ester-fractionation, and it seems certain that a lead salt separation and possibly other refinements are necessary if the amounts of the individual saturated acids are required. It is now definitely established,[4] however, that, although the total percentage of saturated acids can vary within fairly wide limits (*e.g.* from about 40 to 50 per cent. of the total fatty acids), the alteration is due almost entirely to variations in the content of stearic acid, and that the content of palmitic (with myristic) acid always lies, in pig depot fats, within the limits of 29 ± 3 per cent. (wt.).

The acids returned as "undetermined" in the shortened method are actually those not recorded as unsaturated C_{20-22} acids in the determination of ether-insoluble bromo-derivatives. They may include portions of the hexadecenoic and myristic acids of the fats; but it should be borne in mind that, as pointed out earlier, the separation afforded by the procedure described cannot be considered quantitative. The method is offered as one which gives a good, albeit somewhat empirical, approximation to accuracy in the final data obtained, and not as a separation equal in accuracy to that obtainable by the full ester-fractionation procedure.

Our thanks are accorded to the Department of Scientific and Industrial Research for permission to publish the above results.

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The Analysis of Aliphatic and Aromatic Thiocyanates

By W. E. KEMP

THE increasing development and use of alkyl thiocyanates as insecticides present a new problem in analysis for chemists who have to deal with the evaluation of insecticides in their work. Perusal of the literature reveals that few, if any, methods for the analysis of these have been published. The following work was therefore undertaken.

At the outset it may be mentioned that the field for analysis is considerably narrowed by the fact that only a few organic thiocyanates have been found to have practical value as insecticides. The only ones that I have found in sprays on the market in Canada and the U.S.A. are the following:—β-Butoxy-β-thiocyano-diethyl ether, lauryl thiocyanate, 3-thiocyanopropyl phenyl ether, trimethylene dithiocyanate, α-naphthyl isothiocyanate and *m*-phenylene di-isothiocyanate. Of these, the first four fall into Group A (*infra*). Thus, in actual practice, only the last two fall into the second group, and are the only members of this group likely to be found. The first and fifth in the list are sold commercially as "Lethane 384" and "Kesscocide 95," and are those most usually found. Field tests on cockroaches appear to indicate that the thiocyanates in Group A have a more rapid paralysing action than those in Group B.

Determination of the nitrogen and sulphur contents of the petroleum spray and subsequent calculation to the alkyl thiocyanate present is the usual procedure employed in the analysis of these insecticides. This method of analysis had been in use for only a short period when three serious objections developed: first, it is obvious that the calculations hold good only when the particular alkyl thiocyanate present is known; secondly, even when the thiocyanate is known, other nitrogen and sulphur compounds present may interfere; thirdly, the complete analysis takes a considerable time.

THEORETICAL.—Hydrolysis of alkyl thiocyanates takes place fairly easily with alkalis, and this reaction was studied with a view to its utilisation for the determination of alkyl thiocyanates in terms of cyanogen.

Thiocyanate insecticides containing either an aliphatic or an aromatic group can for the purposes of analysis be roughly divided into two main divisions. Those with normal thiocyanic acid, $HS - C \equiv N$, and those with isothiocyanic acid, $NH = C = S$, in the molecule.

The first group, "A," those containing the normal thiocyanogen radical, are hydrolysed as follows: $2R\text{SCN} + 2\text{KOH} = \text{KOCN} + \text{KCN} + H_2O + 2R\text{S}$, where *R* represents the alkyl or aromatic group. It also appears that some side reactions take place with the formation of sulphides in addition to the thio-ethers.

The second group, "B," is hydrolysed into the primary amine as follows: $R - N = C = S + 3\text{KOH} = R\text{NH}_2 + \text{K.SH} + K_2CO_3$.

The difference between the products of the hydrolysis of the two groups, giving the first preliminary separation, also divides the analysis of the insecticide into two types. It was found possible with Group "A" to evaluate the insecticide in terms of cyanogen only, without differentiating between the alkyl or aromatic groups.

Insecticides falling into Group "B" may be identified by means of qualitative tests for the primary amine resulting from the hydrolysis.* This may, in some instances, be determined quantitatively by the usual methods and the amount of isothiocyanic acid with which it had been in combination then calculated.

As the potassium hydrosulphide formed during the hydrolysis of this group begins to decompose almost immediately in the water present, with the production of hydrogen sulphide, it is not possible to determine it.

EXPERIMENTAL METHODS.—The usual methods for the macro quantitative determination of the hydrolysis product resulting from the decomposition of Group "A" are unsatisfactory when applied to the determination of the quantities involved. The Prussian blue, dinitrosalicylate, picrolonic acid, picric acid and phenolphthalin-phenolphthalein reactions were studied.

The formation of Prussian blue[1] by the cyanogen radical was investigated to see if the cyanide formed by the hydrolysis of Group "A" compounds could be estimated in that way. The ferrous sulphate—ferric chloride and ferrous sulphate—ferric sulphate reactions, followed or accompanied by acidification with hydrochloric or phosphoric acids may be used. The precipitate of Prussian blue can be kept in colloidal suspension with gum ghatti, as recommended by Folin for the estimation of reducing sugars. While these reactions proved valuable for qualitative analysis, I found that the interference from the cyanate present in equal moles and the varying colloid particle size of the Prussian blue influenced the colour when diluted, uncontrollable shades of green or blue being formed. At present this reaction is considered unsuitable for quantitative work.

The reaction between cyanide and dinitrosalicylic acid with production of a red compound is not of sufficient sensitivity.

The combining of alkaline picrate with cyanide[2,3] to give a red, alkaline salt of nitro-amino phenol, when the picrate is in excess, has been reported. A survey of this cyanide reaction has shown it to be suitable for this determination. Other compounds stated by Chapman[2] also to develop colour with this reagent do not interfere under the conditions of test.

Hydrolysis of aliphatic normal thiocyanates by alcoholic caustic potash or soda takes place with or without application of heat. Hydrolysis of aromatic normal or iso-thiocyanates usually requires the application of moderate heat. Hydrolysis of Group "A" at temperatures exceeding 50° C., however, leads to decomposition of the cyanide present. This can be seen by the following experimental results:—

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* *Test for a-naphthylamine.*—Pipette 1 ml. of the alcoholic solution resulting from the qualitative hydrolysis into a test-tube and acidify with glacial acetic acid. Add 2 ml. of a 0·5 per cent. solution of sulphanilic acid in 10 per cent. acetic acid containing a few freshly dissolved crystals of sodium nitrite. The production of a brilliant red colour constitutes a positive test for α-naphthylamine.

Test for m*-phenylenediamine.*—One ml. of the solution from the qualitative hydrolysis is acidified in a test-tube with glacial acetic acid. Upon the addition of a few crystals of sodium nitrite, the presence of *m*-phenylenediamine is shown by the production of a deep yellow colour.

Minutes	Percentage hydrolysis at 20° C.	40° C.	100° C.
1	—	—	89·66
5	24·27	30·52	70·67
15	84·37	90·14	—
30	100·00	100·00	64·90
45	100·00	99·51	63·22
60	100·00	98·55	58·00

It is seen that with digestion at an elevated temperature progressive decomposition takes place as the time of digestion increases. At 40° C. hydrolysis is complete after 30 minutes, further digestion resulting in a gradual decomposition of the cyanide formed. Digestion at room temperature is also complete after 30 minutes; no decomposition takes place on further digestion—up to one hour.

The following procedures have been worked out for the analysis of petroleum base insecticides containing aliphatic or aromatic normal and iso-thiocyanates.

METHOD OF ANALYSIS

SPECIAL REAGENTS.—(1) Approx. *N* potassium hydroxide solution in 80 per cent. ethyl alcohol.

(2) *Trinitrophenol.*—Saturated solution. The crystals used (reagent quality) should contain 10 per cent. of water.

(3) *Picrolonic acid.*—Saturated solution.

(4) *Ferrous sulphate solution.*—Ten g. of the crystalline salt per litre.

(5) *Strong standard cyanide solution.*—Dissolve 25 g. of sodium hydroxide in about 500 ml. of water, cool and transfer to a 1-litre graduated flask. Weigh out 5 g. of sodium cyanide (reagent quality) and transfer to the flask with recently boiled and cooled water, mix well and make to the mark with CO_2-free water. Determine the cyanogen-content per ml. by the standard Liebig method, using potassium iodide and ammonia.

(6) *Cyanide standard for test* (containing 0·00005 g. of CN per ml.).—Run the calculated amount (usually about 20 ml.) of strong cyanide solution (5) from a burette into a 1-litre graduated flask containing 10 g. of sodium hydroxide and 500 ml. of water. Make up to the mark with CO_2-free water. This solution, if properly made, will not alter in strength for 2 or 3 weeks when protected from carbon dioxide and acid fumes.

(7) *Alkaline picrate solution.*—Prepared by saturating a 3 per cent. solution of sodium hydroxide with picric acid, leaving for 12 hours and filtering off the precipitated crystals. The solution will keep for 15 to 20 days in the dark.

(8) *Caustic solvent.*—Dissolve 40 g. of sodium hydroxide pellets in exactly 280 ml. of water, cool, transfer to a 1-litre graduated flask with 600 ml. of ethyl alcohol and then add 30 ml. of diethylene oxide (reagent quality). The final solution should not be cloudy; if it shows a turbidity, water should be added in 2-ml. portions, until it becomes clear.

Special apparatus.—Benedict sugar-tubes graduated at 25 ml.; Ostwald-Folin pipettes (3, 5 and 10 ml.) calibrated for blowing out; cylindrical separating funnels of 150 ml. capacity.

QUALITATIVE HYDROLYSIS.—Put 10 ml. of the insecticide into a large Pyrex test-tube. Add 10 ml. of the alcoholic potash (the caustic solvent must not be used) and shake well to mix. Heat rapidly to boiling, with vigorous shaking. Remove, transfer to a centrifuge tube and centrifuge until the two layers separate. Pipette 1 ml. of the bottom (alcoholic) layer into a Benedict sugar-tube graduated at 25 ml. Add 3 ml. of the picrate solution and observe the colour. Boil over a free flame for 5 minutes. Remove and again note the colour.

If the insecticide contained aliphatic or aromatic normal or isothiocyanates, the following colour reactions may occur:

I. A bright blood red colour is produced on adding the picrate and disappears on heating, the colour changing to the normal deep yellow or orange. This indicates a primary amine and shows that the insecticide contained an isothiocyanate.

II. No immediate colour change occurs, but after heating a deep, almost purple-red colour is produced. This indicates the presence of the cyanogen radical, and the insecticide contained a normal thiocyanate.

III. If there is an immediate blood-red colour, which persists and grows darker on heating, the presence of both iso and normal thiocyanates is indicated.

IV. No colour is produced. The insecticide does not contain any aliphatic or aromatic normal or isothiocyanates.

Any positive reactions given by the above test should be confirmed and amplified by the following tests.

Picrolonic acid test for Reaction I.—Take a further 1-ml. portion of the digested sample, add 3 ml. of the picrolonic acid reagent and heat in the boiling water-bath for 10 minutes. A deep red colour observed on looking down through the solution indicates isothiocyanates. This test is also given by normal thiocyanates and can be used only in the absence of a positive Prussian blue test. If the Prussian blue test was positive, Hofmann's test[4] for primary amines, commonly called the mustard oil or carbylamine test, should be used.

Prussian blue test for Reaction II.—Put 2 ml. of the alcoholic extract into a large test-tube. Run in, with shaking, 3 ml. of the ferrous sulphate solution. Mix well and boil over a free flame, shaking meanwhile, for 5 minutes. Make slightly acid with dilute hydrochloric acid. A deep blue colour, remaining blue or greenish upon dilution to 25 ml., constitutes a positive test for Group "A" in absence of free aldehydes.

QUANTITATIVE ANALYSIS OF GROUP "A" (in absence of Group "B").—Pipette 10 ml. of the insecticide spray, by means of an Ostwald-Folin pipette, into a 150-ml. glass-stoppered cylindrical separating funnel. Run in 75 ml. of the caustic solvent. Heat carefully to 40° C. (not higher), and shake vigorously at between 30° to 40° C. for 30 minutes. Unstopper, and allow the two layers to separate. Run off the solvent layer into a 250-ml. beaker, and rinse down the funnel with four 10-ml. portions of 1 per cent. aqueous sodium hydroxide solution, shaking well after each addition and transferring each portion to the beaker. Add to the contents of the beaker 1 g. of "Filtercel" or dry asbestos fibre and mix well. Filter into a 250-ml. graduated flask through Whatman No. 31 paper. Rinse down the funnel, wash the filter-paper and its contents well, and make up to the mark with 1 per cent. aqueous sodium hydroxide solution. The resulting solution will probably be cloudy and opalescent, but this will not interfere with the determination. The flask will then contain all the available cyanogen from 10 ml. of spray.

Introduce 3 ml. of the prepared solution into a Benedict sugar-tube, using an Ostwald-Folin pipette. Place 3 ml. of the standard cyanide test solution in a second tube marked "S." Introduce 5 ml. of the trinitrophenol solution into each tube. Transfer the tubes to a boiling water-bath and heat for 10 minutes, shaking the tubes several times during the heating period. Remove, cool, make up to mark with water, and filter the unknown and standard solutions into Duboscq cups through Whatman No. 44 paper. The filtered solution should be clear. Place the cups in a colorimeter of the Duboscq type, and set the standard at 10 or 20 mm. depth depending upon the colour. Viewed through the eyepiece of the instrument the colour should be deep yellow; depths that give an orange or red shade should be avoided, as they make colour matching more difficult. After setting the standard, adjust the unknown solution in the usual manner until the colours match.

Calculation.—This is effected as follows:

$$\frac{100 \times \left(\dfrac{\text{reading of standard} \times \text{strength of standard}}{\text{reading of unknown}}\right)\left(\dfrac{250}{\text{aliquot part}}\right)}{10 \times \text{specific gravity of sample}}$$

$$= \text{available cyanogen per cent. of sample}$$

As the hydrolysis gave equal moles of cyanate and cyanide, as shown by the preceding equation, the percentage of CN available × 2 is equal to the total amount of cyanogen present.

The aliquot portion of prepared solution taken for the colour matching is varied in accordance with the amount of cyanogen present in order to have sufficient cyanide present for the colour reaction.

The following table illustrates the accuracy obtained by this procedure in analysing a 5 per cent. kerosene solution of two commercial aliphatic thiocyanates.

CN present (by calculation), per cent. ..	0·32	0·32	0·32	0·32	0·32	0·16	0·16	0·16	0·16	0·16
CN found, per cent. ..	0·299	0·318	0·320	0·320	0·323	0·1618	0·1610	0·1620	0·1600	0·1599

SUMMARY.—A colorimetric procedure for the evaluation of normal aliphatic and aromatic thiocyanate insecticides in terms of cyanogen has been devised. It is suggested that the most satisfactory method available for the quantitative determination of isothiocyanates is the utilisation of the same hydrolysis reaction used in the determination of the normal thiocyanates and the subsequent determination of the primary amine. The isothiocyanates are easily identified qualitatively by the usual tests for the primary amine.

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The Indigo-Carmine Reaction as a Test for Chlorates and Hypochlorites in Milk

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REQUIRING methods of detecting traces of chlorates in soils and plant tissues, I have studied the indigo-carmine reaction reported by Korenman[1] and have developed it into a satisfactory test for such purposes.[2] The test is not specific for chlorates, but is also sensitive to other oxidising agents. The need for a similar test for chlorates and hypochlorites in milk was brought to my notice, and the results of the application of the indigo-carmine test to the examination of milk are here reported.

Wright and Anderson[3] have laid stress upon this need for a sensitive test as one of the pre-requisites to a revision of the legislation relating to the sterilisation of dairy equipment. In this country the chemical sterilisation of dairy equipment, apart from milking machines, is prohibited, the principal reason being the difficulty of detecting intentional or accidental contamination of milk with the sterilising chemical through inefficient or inadequate rinsing. Chemical sterilisation of all dairy utensils is legal in Canada, and Lockhead[4] has reported on the effectiveness of chlorine compounds in sterilising milk-cans, and has shown that for general sterilisation they are more efficient than the frequently inadequate supplies of hot water and steam.

Rupp's test[5] by which 20 p.p.m. of chlorine can be detected is the only published test in which the reactant is the chlorine itself. The test published by Wright and Anderson[3] and the one here published both detect hypochlorite indirectly by the chlorate present as an impurity. Keister[6] has shown that the Rupp test is extremely sensitive to copper, which is a normal constituent of milk to the extent of 0·2 p.p.m., and which, as Mattick[7] has shown, may be increased by the milk coming into contact with copper or damaged tinned copper. The test described by Wright and Anderson involves the use of ice, a centrifuge and a mercury vapour lamp, which are not always available, whereas the test here published can be carried out with very simple apparatus.

Even though the indigo-carmine reaction is an indirect indication of the presence of hypochlorite, its sensitivity to chlorate is such that smaller traces of hypochlorite can be detected than is possible with the Rupp test. Hypochlorites from various sources were all found to contain chlorate, which is apparently a normal impurity with the present methods of hypochlorite manufacture.

REAGENTS.—The solutions used were as follows:

(1) *Aqueous sodium sulphite solution.*—Twenty g. of the anhydrous salt are dissolved in 100 ml. of water. Korenman recommends a saturated solution, but it is not so stable as the one now recommended.

(2) *Hydrochloric acid* (3 *N*).—Thirty-eight ml. of concentrated acid made up to 100 ml. with water.

(3) *Aqueous indigo-carmine solution* (0·02 per cent.).—(B.D.H. biologically tested standard stain was used in these tests.)

Mixtures of these solutions required for tests must be prepared immediately before use, owing to rapid decomposition and decolorisation after admixture. The mixtures may be made by measurement from self-filling micro-burettes, convenient sizes for the three solutions being 2 ml. capacity graduated in 1/100 ml. for the indigo-carmine solution, and 5 ml. capacity graduated in 1/20 ml. for the other two solutions.

THE TEST.—This depends on the fact that a mixture of the above reagents is decolorised by chlorates and certain other oxidising agents. The decolorisation also takes place in air, but much more slowly than in presence of specific oxidising agents. The proportion of the three solutions and the quantity of indigo-carmine in the mixture has a pronounced effect on the sensitivity. The reaction is a time-reaction, and the time varies with the quantities of chlorate and indigo-carmine in the mixture. Increase of chlorate decreases reaction time, whilst increase of indigo-carmine increases the reaction time and reduces the sensitivity.

Since decolorisation takes place even when no chlorate or hypochlorite is present, it is necessary to compare the reaction of a control milk with that of the test sample by timing or otherwise observing the rate of colour discharge. The decolorisation of the dye by a chlorate-containing milk is very rapid, being complete in a few seconds or, at most, two or three minutes, whereas samples containing no chlorate take from an hour and a half to two hours for all colour to be discharged.

Various proportions of the three solutions were tried and rejected because of reduced sensitivity of the reagents, too rapid decolorisation of the dye in control milks, or an insufficient intensity (and therefore perceptibility) of blue coloration at the beginning of the reaction. The mixture finally adopted consists of 0·5 ml. of sodium sulphite solution, 0·8 ml. of hydrochloric acid, and 0·04 ml. of indigo-carmine solution. The procedure is as follows:

(1) Measure into test-tubes 1 ml. of control (fresh untreated) milk and 1 ml. of the milk to be tested.

(2) Add to the control milk the sodium sulphite, hydrochloric acid and indigo-carmine successively. Note the time or start a stop-watch, and allow the tube to stand in a white painted test-tube rack. The mixture should remain blue for about an hour and a half.

(3) Add the same quantities of the same chemicals to the tube of milk requiring testing. The stop-watch should be used to note the time taken for colour discharge. This tube should be placed in the test-tube rack for comparison with the control tube. Other samples of milk can be tested simultaneously and compared with the same control.

Experimental Results.—*Sensitivity to chlorate.*—The test was found to be extremely sensitive to aqueous solutions of chlorate and reacted with 0·00012 mg. of sodium chlorate. It was not quite so sensitive in milk, but reacted with 0·0005 mg. in 1 ml. of fresh milk (0·5 p.p.m.).

Sensitivity to hypochlorite.—In aqueous solutions hypochlorite reacted with indicator mixtures from which the sodium sulphite was omitted, but when hypochlorite was mixed with milk, decolorisation took place only when all three reagents were present in the indicator mixture. The reaction obtained was due to the chlorate present in the hypochlorite solution.

The hypochlorite solution used in the experiment was found to contain 2·3 per cent. of sodium hypochlorite and 0·08 per cent. of sodium chlorate. Mixtures with milk were prepared to contain from 10 to 50 p.p.m. of sodium hypochlorite, and a positive reaction was obtained with all solutions containing more than 15 p.p.m. of sodium hypochlorite in 1 ml. of milk. This is equivalent to a sensitivity limit of 7 to 7·5 p.p.m. of available chlorine. The results of the analysis of the hypochlorite solution show the sensitivity limit of 15 p.p.m. of sodium hypochlorite to be the equivalent of a sensitivity of 0·52 p.p.m. of sodium chlorate. A similar sensitivity limit was found with mixtures of pure sodium chlorate in milk (0·5 p.p.m. of sodium chlorate); this indicates that the reactant in a hypochlorite/milk mixture is sodium chlorate.

The sensitivity limit of 15 p.p.m. of sodium hypochlorite will not necessarily be the sensitivity limit for all hypochlorite solutions. The limit depends entirely on the proportion of chlorate present, and this will vary with the age of the hypochlorite solution and with the method of manufacture. It is unlikely that under present methods of manufacture commercial hypochlorite solutions containing no sodium chlorate could be obtained. Hypochlorite from various sources was examined and found to contain enough chlorate to make detection easy.

Effect of Temperature and Duration of Storage of Milk on the Sensitivity of the Test.—In order to ascertain whether storage time and temperature would affect the sensitivity of the reaction, milks containing various quantities of sodium hypochlorite were prepared, kept at different temperatures, and tested at intervals (see Table I). The temperatures selected were 16° C. (room temperature), 0° C. (minimum bacterial activity), and 32° C. (maximum bacterial activity). At room temperature there was a gradual reduction in sensitivity, but after 48 hours it was still possible to detect chlorate in the milk prepared to contain 20 p.p.m. of sodium hypochlorite, but only by taking 2 ml. of milk for testing instead of the usual 1 ml. On curdling, which had taken place after 72 hours, it was only possible to detect chlorate in the milk sample to which 50 p.p.m. of sodium hypochlorite had been added, and 24 hours after curdling no chlorate could be detected in this sample. At 0° C. sensitivity was fully maintained for five or more days. At 32° C. curdling took place in 28 hours and, although there was no reduced sensitivity after 20 hours, no trace of chlorate could be detected after 28 hours when the milk had curdled.

This reduction in sensitivity when milk is curdled might be due to bacterial decomposition of the chlorate or to a reaction between the chlorate and bacterial metabolic products. The former is the more probable, and evidence in support of this was obtained by observations on the duration of sensitivity in milks to which chlorate was added after curdling. Rapid disappearance of the chlorate was noted in such milks, but if the sample was steam-sterilised for 30 minutes at 100° C. before the chlorate was added, detection of chlorate by this method remained possible for an indefinite period.

TABLE I

EFFECT OF TIME AND TEMPERATURE ON THE SENSITIVITY OF INDIGO-CARMINE TO SODIUM HYPOCHLORITE IN MILK

+ = Positive reaction to indigo-carmine test.
— = Negative ,, ,,

Temperature	Time (in hours) after preparation	Quantity of milk used for test ml.	Parts per million of sodium hypochlorite in milk				
			50	30	25	20	15
16° C. (room temperature).	0	1	+	+	+	+	+
		2	+	+	+	+	+
	24	1	+	+	—	—	—
		2	+	+	+	+	—
	48	1	+	—	—	—	—
		2	+	+	+	+	—
	72*	1	+	—	—	—	—
		2	+	—	—	—	—
	96	1	—	—	—	—	—
		2	—	—	—	—	—
0° C. (minimum bacterial activity).	0	1	+	+	+	+	+
		2	+	+	+	+	+
	24	1	+	+	+	+	+
		2	+	+	+	+	+
	48	1	+	+	+	+	+
		2	+	+	+	+	+
	72	1	+	+	+	+	+
		2	+	+	+	+	+
	96	1	+	+	+	+	+
		2	+	+	+	+	+
	120	1	+	+	+	+	+
		2	+	+	+	+	+
32° C. (maximum bacterial activity).	0	1	+	+	+	+	
		2	+	+	+	+	
	20	1	+	+	+	+	
		2	+	+	+	+	
	28*	1	—	—	—	—	
		2	—	—	—	—	

* Time in which milk curdled.

Since the test does not detect hypochlorite directly, the implications to be deduced from test results must be considered carefully. A milk sample which gives a positive reaction can only be assumed to contain chlorate, and there is no positive proof of the presence of hypochlorite.

A positive reaction, consisting of colour discharge within fifteen minutes, is not found in pure unadulterated milks and consequently can be assumed to be due to addition of chlorate or a preservative chemical, such as sodium hypochlorite, which contains chlorate as an impurity.

A negative reaction, consisting of colour discharge in over fifteen minutes, will indicate less than 0·5 p.p.m. of sodium chlorate.

SUMMARY.—A test is described capable of directly detecting 0·5 p.p.m. of sodium chlorate in 1 ml. of milk and of indirectly detecting sodium hypochlorite according to the quantity of sodium chlorate present as impurity. The degree of sensitivity obtained to sodium hypochlorite used in the experiments described was 15 p.p.m. of sodium hypochlorite and 7 to 7·5 p.p.m. of available chlorine. The sensitivity is maintained for at least five days if the milk is kept in a refrigerator, but there is a gradual reduction in sensitivity when the sample is kept at room temperature, and it is advisable to keep samples at as low a temperature as possible during transport.

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The Determination of Arsenic by a Continuous Electrolytic Method*

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AT intervals during recent years I have attempted to design for arsenic determinations an electrolytic apparatus that would work continuously for half-a-day—or longer, if necessary—without having to be dismantled. The underlying principle was to ensure a rapid method for the examination of those substances which long experience had shown to be, almost invariably, free from arsenic. Naturally, the appearance of more than the slightest trace in the deposit tube in such cases would be regarded with suspicion, necessitating further investigation and corroboration. Moreover, it has been established that, in the electrolytic methods evolved from the work of Thorpe,[1] Wilkie,[2] Monier-Williams[3] and others, the porous pot tires and becomes insensitive after two or three determinations in sequence, whereas the use of parchment as a membrane, as practised by Trotman,[4] Sand and Hackford[5] and Callan and Parry Jones,[6] gives only indifferent results. The sensitivity usually returns after washing, drying and allowing to stand for a day, but the porous pots require very careful attention. The apparatus is also of very small capacity and consequently only one substance can be tested, after which it is necessary to dismantle and start again, unless the test liquid is removed by suction and replaced, as practised by Aumonier.[7] Hence one soon reaches the limit of the number of tests per day with each appliance, owing to the tiring of the porous pot and the time required for each test, although the former objection is mainly overcome by the adoption of porous pots fitted with interchangeable ground-glass joints. The porous-pot method is capable of good results, but the apparatus must not be overworked and considerable experience is required before competence is attained.

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Statistical examination of our arsenic results on "buying" samples and consignments of raw food materials for a period of 12 months showed the following:

TABLE I

Proportion of materials.	Arsenic
94·5 per cent.	Nil, *i.e.* no deposit in tube.
4·0 ,, ,,	From 1/400 to 1/100 grain per lb.
1·5 ,, ,,	More than 1/100 grain per lb.

The foregoing results did not include gelatin, as this commodity generally contains a trace of arsenic, and wrapping materials are more conveniently examined by the Marsh–Berzelius method.

The advantage of a rapid continuous process is very evident when one considers that such a small proportion of foodstuffs contained arsenic in a determinable amount, and only a quarter of these in amounts above the limit of 1/100 grain per lb.

THE CONTINUOUS ELECTROLYTIC METHOD.—*Description of Generating Apparatus.*—The apparatus is made of glass in one piece, as shown in Fig. 1. The glass tubing used for the electrolysis compartments is 1/2 to 9/16 inch in internal diameter, while the exhaust tube E is 3/16 of an inch. The design of the apparatus ensures a steady flow of the test liquid over the cadmium cathode, so that any arsenic is liberated continuously. The test liquid is introduced at the bottom of the cathode compartment and, being made as dense as or slightly denser than the acid electrolyte already present, it diffuses slowly past the cathode. The excess of liquid passes through the plug of glass-wool in tube B into the anode compartment A, and finally, with the liberated oxygen, down the exhaust tube E to waste. The tap-funnel D, holding 15 ml., is graduated in 2·5 ml., so that this quantity can be admitted at short intervals, if the semi-automatic feed—described later—is not attached. The tube B continues a short distance beyond the anode compartment, enabling the glass-wool packing to be easily fitted and renewed when necessary. This tube B is closed with a rubber bung when the apparatus is in use. The exhaust tube E is situated a short distance above B, so that the latter is always full of electrolyte. The small tap funnel F is used for the introduction of 1 ml. of amyl alcohol when frothing occurs.

The Electrodes.—The cathode consists of a narrow cylinder of cadmium, 1¼ inch long and 3/8 inch in diameter. This is tapered and tapped at one end and screws on to a 3/16-inch brass rod. The latter passes through a glass tube sealed to the hollow stopper and a small piece of rubber tubing is fitted over the tapered end of the cadmium electrode and pushed inside the glass tube. In this way the junction is protected from acid, and the small amount of rubber exposed is of no consequence. The top of the brass rod screws into a wider piece of brass rod, which is hollowed to take a single pin for making the necessary electrical contact. The wider piece of brass rod is kept central by means of a rubber bung which fits inside the hollow glass stopper. It is of paramount importance that the electrode be centrally situated in the cathode compartment, and this will be so only if the glass tube from the hollow stopper is central. The cathode also must be of sufficient length practically to touch the bottom of its compartment, but when it has been correctly fitted, no further adjustment is necessary.

A similar type of cathode can be made by covering the brass rod with rubber tubing which would also fit over the tapered end of the cadmium electrode, thereby protecting the junction. The brass rod would pass through a rubber bung and be suitably connected with the negative of current supply, care being taken to insulate the terminal. In this way the ground joint is eliminated, but it is then necessary to keep the electrode central by means of a circular baffle plate made of fairly stout celluloid. The baffle plate acts as a guide and is fixed on the protecting rubber tube about 1 inch above the normal level of the electrolyte. The use of rubber bungs and tubing may, at first sight, appear objectionable, but, as in practice no arsenic or antimony deposit is given in a blank test when run for one hour, their adoption can be considered satisfactory.

The anode consists of a small piece of platinum foil or gauze joined to a fairly stout piece of platinum wire which passes through a rubber bung and is connected with the positive of the current supply, the connection being insulated.

The apparatus, by immersion in a trough of water, will stand a current of 2 amps. off the 220-volt D.C. mains, after passing through four half-amp. carbon lamps in parallel, or other suitable resistance. If a lower voltage can be easily arranged, it has the advantage of preventing overheating when the apparatus is left unattended for a long period. The potential difference between the two electrodes is about 15 volts.

Drying the liberated Gas.—The hydrogen generated is passed through a short drying-tube, about 3 inches long, containing mainly cotton-wool but having two short plugs of lead acetate wool, as shown in Fig. 1, to remove hydrogen sulphide. The tube must be packed very lightly, as any pressure here will cause the electrolyte to be expelled from the apparatus. This type of drying-tube is found to be very efficacious,[8] and need only be changed after every two hours' running, or after four determinations.

Deposition of the Arsenic.—The arsenic is deposited according to the Berzelius method with the following precautions:—The arsenic tube is drawn from Jena hard glass tubing, so that the diameter at the point of deposition is 0·075 ± 0·005 inch. The tube, however, is not constricted immediately before the heated portion, as this offers no advantage; in fact, it is a disadvantage, as the gauze cannot be made to fit sufficiently close to the glass. In practice an oblong piece of wire gauze is folded round the tapering part of the deposit tube in a single thickness. The ends are brought face to face and, when in the flame, are left pointing upwards on top of the deposit tube. In this way the gauze fits the shape of the glass and helps in obtaining uniform deposits. The small Meker burner is fitted with a support made either from sheet metal or from a tube of suitable size split down one edge, so that it grips the top of the burner, as shown in Fig. 1. Two upright supports, having semicircular guides, hold the arsenic deposit tube. The gauze, which is heated just to redness, is of sufficient width to fit comfortably between these guides. At a half to three-quarters of an inch from the heated gauze the tube is cooled by a piece of lint dipping into a dish of distilled water. The arsenic tends to deposit in two modifications—brown and grey, and the cooling is to prevent too great a scattering of the grey arsenic, which is appreciably the more volatile variety.

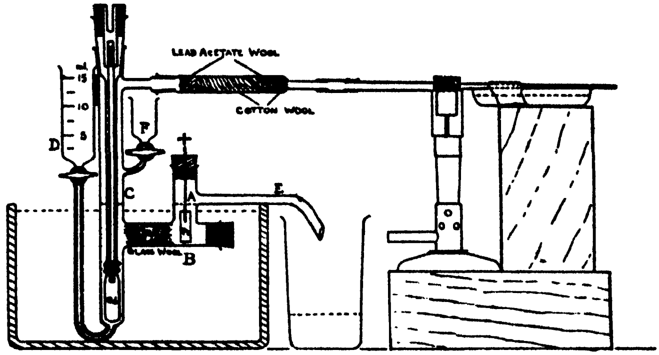
CONTINUOUS ELECTROLYTIC-ARSENIC APPARATUS

Fig. 1

The Electrolyte.—This continuous electrolytic method owes its efficiency to some extent to the use of hydroxylamine as a reducer. A litre of electrolyte is prepared in the following manner:

Reagent A.—Ten g. of hydroxylamine sulphate are dissolved in 900 ml. of distilled water and 200 ml. of arsenic-free sulphuric acid are added. The solution is boiled for a few minutes and cooled, and, if necessary, the volume is adjusted to one litre by the addition of freshly boiled distilled water. If hydroxylamine hydrochloride is the salt available, the hydrochloric acid is removed by heating with conc. arsenic-free sulphuric acid until there is no more effervescence.

Reagent B.—A 10 per cent. hydroxylamine sulphate solution in 50 per cent. arsenic-free sulphuric acid is also prepared for addition to those test solutions prepared after charring, in order to increase the acid content. This solution is referred to later as Reagent B.

Conducting the Determination.—Before each series of tests the cadmium electrode is polished with No. 0 emery cloth to remove any undesirable metallic deposit, such as tin, etc., from previous tests. The electrode is wiped with a clean dry cloth, and the current is switched on as soon as possible after insertion of the electrode in the apparatus, which has been charged with about 15 ml. of Reagent A.

The burner is lighted after a few minutes' running, heating the gauze to redness, and if any doubt exists as to the purity of the components a blank test is made for ten minutes. In the course of some hundreds of tests no arsenic has ever been evolved during the blank test. The test solution is prepared by one of the standard methods, depending on the nature of the commodity. If it is the aqueous extract from a charred residue, it is reduced in volume to the minimum convenient quantity, and, when it is cold, 2 ml. of Reagent B are added. The test solution is transferred to the funnel of the apparatus with a little electrolyte; for convenience the total volume should not exceed 10 ml., although for sugars a volume of 15 ml. is found to be necessary to prevent overheating.

Prior to introducing the solution to the funnel, in a sequence of determinations, 2·5 ml. of water are run into the apparatus to lower the density of the electrolyte, so that the test solution has to diffuse slowly from the bottom of the cathode compartment C.

The test solution is added, 2·5 ml. at a time, at intervals of at least two minutes, and is followed by 5 ml. of Reagent A at the same rate. Alternatively, the test solution can be admitted at an equivalent rate by using the semi-automatic device described below. The test solution can thus be introduced completely in ten to twenty minutes, and the presence of arsenic is readily detected by this time. If arsenic is present, by continuing the test for a further ten minutes all the hydrogen in which arsine is present will have been expelled. When dealing with arsenic-free substances it is possible to obtain three or four results in one hour, whilst when arsenic is present half-an-hour for each is ample.

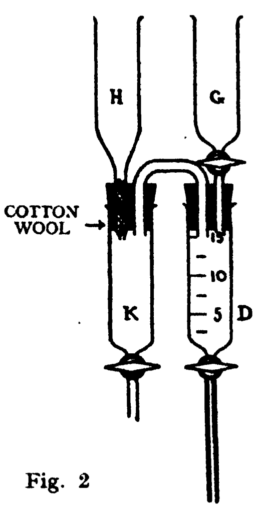

Fig. 2

After two hours' continuous running the drying-tube should be repacked without disconnecting the apparatus and obviously it is desirable to fit a new arsenic-deposit tube after each positive result. In the event of obtaining negative results, it is advisable to test the apparatus occasionally by adding, say, the equivalent of 1/200 grain of arsenic per lb. in 5 ml. of standard electrolyte and treating this as a test solution. Slightly low results are sometimes obtained, particularly after testing phosphoric acid, and this effect has been previously noted by Monier-Williams[3] when testing phosphates by an electrolytic method. The apparatus, however, recovers on further running or after removal and cleaning of the cathode.

After the final test, the cathode must be removed immediately the current is switched off, and should be washed and dried. Only in exceptional circumstances is it necessary to empty the electrolyte out of the apparatus.

Semi-Automatic Feed.—This device fits in the top of the supply funnel (D in Fig. 1), as shown in Fig. 2. H is a funnel with the outlet slightly tapered and lightly closed with a plug of cotton-wool which regulates the rate of water entering K. The solution to be tested is transferred to G and made to enter D by opening the taps of G and K. The taps of G and K are then closed, and the tap of D is opened. The test solution then enters the apparatus according to the rate of entry of water through the plug of cotton-wool; the tightness of packing can be readily adjusted, by using a dental probe or similar implement, to allow the passage of 1 drop in 2 to 4 seconds. Obviously, an ordinary needle-valve can be used for controlling the supply if preferred. The water collected in K is emptied when more test solution is added through G. With this device in use the apparatus requires attention approximately every 15 minutes, which gives ample time for the preparation of the next test solution.

Notes on Upkeep.

(1) In some determinations a large amount of hydrogen sulphide is evolved, and the blackening of the second plug of lead acetate wool indicates a risk that sulphur may be carried into the arsenic tube, so that the packing should be changed at the earliest opportunity.

(2) It is essential to remove the cathode from the electrolyte immediately the current is switched off, and the cadmium must be washed and dried and stored dry.

(3) In preparing test solutions great care must be taken to remove free nitric acid, which is very detrimental to the cadmium electrode.

(4) Owing to its construction the apparatus needs more attention than the porous-pot method, and the constant supply of electrolyte is essential. Neglect in this respect will cause overheating and finally arcing in the glass-wool packing; if the apparatus is to be left for more than 15 or 20 minutes the current supply should be reduced to ½ amp. by removal of three lamps from the resistance. The additional care required for the regular supply of test solution may appear at first sight a drawback to the method; it must be emphasised, however, the the required additions constitute an extremely simple operation.

(5) The apparatus must be cooled in a trough of cold water, the arm B being completely submerged. Care must be taken that the rubber bung in tube B fits well, as a slight leak of acid into the water, accompanied by an electrical leak from the anode, would give a positive charge of high potential to the water, as the operator would observe should he happen, while well earthed, to touch the cooling water.

(6) The design of the apparatus ensures a cathodic overvoltage sufficient for the formation of arsine, while the constant flow of liquid from the cathode counteracts endosmosis, which reduces the efficiency in methods employing porous pots.

DETAILS FOR PREPARING TEST SOLUTIONS.—The preparation of test solutions is divided into three main groups, which cover essentially materials used in cocoa, chocolate and confectionery manufacture. It is of paramount importance that any substance containing chlorides be treated with nitric acid, as well as sulphuric acid, to retain the arsenic in the quinquevalent condition. After nitric acid has been used it must be completely expelled by repeated evaporation to dryness with water, and nitrates must not be put into the apparatus.

I. *Material directly soluble in dilute sulphuric acid* (excluding chlorides and nitrates).

(*a*) *Unaffected by dilute sulphuric acid* (excluding sugars). This applies to phosphoric acid, glycerin, tartaric acid, citric acid, cream of tartar, etc. Five g. of the substance, or 3 ml. with phosphoric acid and 4 ml. for glycerin, are dissolved in the prepared electrolyte (Reagent A), and the volume is made up to 10 ml. in the graduated tap-funnel. The solution is then introduced into the apparatus, as previously described. Phosphoric acid is detrimental to the apparatus, and causes the intensity of the stain to be low, so that in a series of tests it should be left to the end, and any arsenic deposit approaching 1/100 grain per lb. should be regarded with suspicion.

(*b*) *Sodium carbonate, sodium bicarbonate, ammonium carbonate, etc.* Owing to the comparatively low solubilities of the sulphates formed, 2·5 g. is a more convenient amount than 5 g.; it should be dissolved in 15 ml. of Reagent A.

(*c*) *Sugars.* Under this heading are included:—Cane and beet sugar, glucose, cane syrup, invert sugar, honey, etc. Five g. are made up to 15 ml. with Reagent A.

II. *Materials requiring charring with sulphuric acid.*

(*a*) *Insoluble food products,* excluding those containing chlorides, *viz.*: "soluble" cocoa, milk, condensed milk or milk chocolate, colours and highly coloured decorations, egg albumen, etc. Five g. of the substance, in a reasonably fine state of division, are mixed in a silica dish with 3 ml. of water (20 ml. for gelatin) and 2 ml. of conc. arsenic-free sulphuric acid. The dish is heated on a sand-bath or sand-tray over a small burner and the contents are occasionally stirred until a spongy char results. The charred mass is broken up with a small glass pestle and extracted three times with boiling water. The combined filtrates are evaporated to 7 or 8 ml. and transferred to the graduated funnel of the apparatus, together with 2 ml. of Reagent B.

It is important that the heating in the silica dish should not be too prolonged, but it must be sufficient to give an aqueous extract the colour of which is not more than a pale yellow. This method has been found satisfactory for all our products except those containing chlorides, which are dealt with as described in III (*a*).

(*b*) *Paper, ribbon, Cellophane* and other wrapping materials, but excluding metal foils:—One g. is heated with 1 ml. of water and 0·5 ml. of conc. sulphuric acid and treated as described above.

III. *Materials requiring nitration.*

(*a*) *Foodstuffs containing chlorides.* Five g. of material are mixed in a silica dish with 4 ml. of conc. (As-free) nitric acid and 2 ml. of sulphuric acid. The dish is carefully heated as before. When no more nitric fumes are evolved the dish is cooled, water is added, and the liquid is evaporated to dryness. The residue is then extracted as described under II (*a*).

(*b*) *Sodium chloride.* The chloride (2·5 g.) is heated with 2 ml. of conc. (As-free) nitric acid and 5 ml. of conc. (As-free) sulphuric acid in a silica basin to expel the hydrogen chloride. The residue is evaporated to dryness with water and then dissolved in Reagent A.

(*c*) *Synthetic colouring substances.* It is common practice for colour manufacturers to adjust the strength of synthetic colours by the addition of sucrose, sodium sulphate, sodium chloride, etc., even to the extent of one part of colour to several parts of diluent. The likelihood of chlorides being present and the liability of certain colours to deflagrate when heated with conc. nitric acid render the following treatment necessary:

The sample (2·5 g.) is mixed in a 3-inch silica dish with 5 ml. of water. Then with continual stirring, 2 ml. of conc. nitric acid are added followed by 2 ml. of conc. sulphuric acid. The dish is heated cautiously at a low temperature on a sand-bath for 1½ to 2 hours, or until no further action is apparent. The dish is cooled and the residue is disintegrated with a glass rod. Three ml. of water are mixed in, followed by 2 ml. of conc. nitric acid and 2 ml. of sulphuric acid, and the heating is repeated. The dry char is made wet with water and reheated to dryness, and the residue is pulverised and extracted with three or four portions of water, as previously described under *Insoluble substances* (*supra*).

EXPERIMENTAL WORK.—*Standard Arsenic Solution.*—This was prepared by dissolving 0·179 g. of pure arsenious oxide in a minimum quantity of sodium hydroxide solution and diluting to one litre. Forty ml. of this solution were further diluted to a litre and gave the standard arsenic solution, 1 ml. of which is equivalent to 1/100 grain per lb. on a 5-gram sample. The alkaline solution was preferred to a slightly acid one, since the latter tended to develop mould. There is little likelihood of the alkali at this extreme dilution dissolving any arsenic from the glass bottle.

The apparatus was found to be sufficiently sensitive to detect 0·1 ml. of the standard arsenic solution in 10 ml. of the electrolyte, equivalent to 1/1000 grain per lb. on a 5-gram sample. The actual weight of arsenious oxide detectable in 10 ml. of solution is, therefore, 0·7μg. It is not recommended to read to such fine limits, and for general requirements it will be quite sufficient to take 1/400 grain per lb. as the lowest limit.

Preparation of Standards.—In preparing standard deposits for future comparison, it has been customary to seal these in an atmosphere of dry hydrogen, as exposure to air causes rapid fading. The mirrors prepared in this way had a useful life of about 6 months and then had to be replaced. The effect of sealing the tubes in an atmosphere of dry carbon dioxide resulted in greatly improved keeping properties, and a set of standards in daily use for over 6 years showed virtually no decrease in intensity.

Tests with the Addition of Arsenic.—The following results in Table II show a typical continuous run with one apparatus carried out in 3½ hours.

As a thorough test, an independent chemist prepared a number of materials by adding arsenic in certain amounts which were not divulged until the materials had been tested by both the porous-pot and continuous methods. The materials

TABLE II

Test No.	Material	Treatment	Arsenic added Grain per lb.	Arsenic detected Grain per lb.
58	5 g. of cocoa	Charring with sulphuric acid	nil	1/1000
59	,, ,, ,,	,, ,, ,, ,,	1/400	1/400
60	Marzipan fruits	Nitrated	nil	1/1000
69	Arsenic only		1/200*	1/200
70	3 ml. of phosphoric acid	+ 7 ml. of Reagent A.	nil	nil
71	,, ,, ,,	,, ,, ,,	1/200	1/250
72	Arsenic only		1/200*	1/200

* 0·5 ml. of dilute standard arsenic solution in 5 ml. of Reagent A.

were all previously tested and found free from arsenic. The amounts thus added "under key" and the amounts found are given in Table III.

TABLE III

ARSENIC TESTS UNDER KEY

No.	Material (5 g.)	Key Grain	Porous-pot method Grain per lb.	Continuous method Grain per lb.
158	Glycerin	1/50	1/40–1/50	1/40
159	Glucose	1/50	1/50–1/65	1/30
160	Cocoa I	1/100	1/100	1/100
161	Cocoa II	1/100	—	1/100
162	Invert sugar ..	1/50	1/50	1/50
163	Phosphoric acid ..	1/50	1/50	1/50

The deposits obtained from the continuous process were generally slightly more intense than those from the porous-pot method, particularly for glucose. The test with this was repeated and gave a deposit exactly similar to that obtained "under key." In determining the arsenic-content of glucose it would be advisable to compare the stain with a standard prepared by using 5 g. of glucose. As commercial glucose is invariably free from arsenic—and has been for some years—this abnormally high deposit is of little consequence. The stains by both processes were judged by the standards prepared by the porous-pot method.

CONCLUSIONS.—The continuous electrolytic apparatus was originally intended to deal with the substances usually free from arsenic. The results obtained by adding known amounts of arsenic, together with those tested under key, compare favourably with those obtained by the more orthodox method. The speed with which any arsenic present can be detected in a series of tests is a point of great importance.

The work done on the preparation of test solutions indicates that the use of nitric acid should be avoided wherever possible and, if charring is necessary, only sulphuric acid should be used except in the presence of chlorides. In testing gelatin it is not sufficient to hydrolyse with dilute sulphuric acid as the gelatin greatly increases the resistance of the continuous apparatus and, as this commodity usually contains arsenic, the porous-pot method has much to recommend it.

The continuous electrolytic apparatus has already been of considerable value and should find application in other food factories where a large number of arsenic tests are made.

The manufacture of the described apparatus has been undertaken by L. V. D. Scorah, Scientific Glass Specialist, King's Norton, Birmingham.

I am greatly indebted to Messrs. Cadbury Bros., Ltd., for permission to publish work carried out in their laboratories at Bournville.

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CHEMISTS' DEPARTMENT
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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE "EVOLUTION" METHOD FOR DETERMINING SULPHUR IN MILD STEEL

THE usual method used for the routine determination of sulphur in mild steel consists in dissolving the steel in hydrochloric acid, passing the evolved gases into ammoniacal cadmium chloride or zinc sulphate solution, filtering off the sulphide precipitate, dissolving it in a known excess of acid iodine solution, and titrating back the excess of iodine.

For rapidity it is often convenient to omit the filtration and to wash the entire contents of the absorption tube directly into the acid iodine; it is stated[1] that "very little error" arises from this procedure. We have found, however, that a considerable error may arise from the volatilisation of iodine consequent upon the warming up of the solution by the heat of neutralisation of the ammonia and the acid iodine solution; but that this error can be entirely eliminated by cooling the acid iodine solution with added ice before the ammoniacal solution is washed in. The recommended procedure is as follows:

Place a 5-g. sample of the mild steel in a 200-ml. flask fitted with a 100-ml. tap-funnel and connected with a wash-tube containing water and thence with an absorption-tube containing 15 ml. of ammoniacal cadmium chloride solution (40 g. of $CdCl_2$ in 1600 ml. of water + 400 ml. of ammonia solution of sp.gr. 0·880). Fill the tap-funnel to the brim with conc. hydrochloric acid, and connect it with a source of carbon dioxide. Run the acid into the flask, replacing it with carbon dioxide. Warm the flask so that gas is steadily evolved; solution should be complete in 30 minutes. When no more gas is evolved, boil the acid for 1 minute, and then pass a stream of carbon dioxide through the apparatus for 2 minutes. Disconnect the absorption tube and wash its contents into a large beaker containing 25 ml. of ice-cold 9 *N* sulphuric acid (480 ml. of conc. acid in 2 litres), 10 ml. of 0·1 *N* potassium iodate solution, 10 ml. of 6 per cent. potassium iodide solution and several pieces of ice. When all the cadmium sulphide has dissolved, dilute the solution to about 400 ml. and titrate with 0·025 *N* sodium thiosulphate solution, freshly made each day from stock 0·1 *N* solution, and standardised against a "blank" of iodate, ammoniacal cadmium chloride, etc., containing no sulphur.

This procedure has been used in many hundreds of analyses, and gives very reproducible results, certainly accurate to within ± 2 of the third decimal place of the result, *e.g.* S per cent. = 0·064 ± 0·002.

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G. E. S. Eyles

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THE DETERMINATION OF CARBON DIOXIDE, WITH SPECIAL REFERENCE TO BAKING POWDER AND SELF-RAISING FLOUR

The apparatus is a slightly modified form of that which we have previously described in connection with the analysis of vinegar.[1] The calcium chloride tube with bulbs is replaced by two similar, but larger tubes (length of limb 8 in. and diameter ⅞ in.), connected by means of a piece of glass tubing, and the thistle safety-funnel is placed in the end limb of the second tube. A convenient size for the distillation flask is 500 ml.

The second tube is necessary, as an appreciable amount of carbon dioxide passes over before the condensation of any liquid takes place and is not all absorbed in the first tube. After about 30 ml. have distilled there is a pressure set up which tends to prevent the last traces of carbon dioxide being swept out of the distillation flask. By interrupting the distillation and replacing the first by the second tube this final sweeping-out may be readily effected.

Determination of Carbon Dioxide in Sodium Carbonate.—Five ml. of 10 per cent. phosphoric acid diluted with 5 ml. of water free from carbon dioxide (all the distilled water used in these determinations was well boiled before use) are placed in the separating funnel, which passes through a bung in the neck of the distillation flask. The carbonate is placed in the distillation flask together with a little pumice and sufficient distilled water to make the volume up to 50 ml. Five ml. of *N* sodium hydroxide solution are measured into the first tube, 1 ml. into the second tube, and sufficient water to form a seal to each tube is added. A few drops of *N* sodium hydroxide solution are placed in the thistle-funnel to act as a "back" trap. The apparatus is assembled, the acid in the separating funnel is run into the distillation flask and the contents are heated slowly until distillation begins. The distillation is continued until about 30 ml. have been collected in the first tube, heating is discontinued, and, when the distillation has ceased, the first tube is disconnected from the condenser and replaced by the second tube as quickly as possible; the glass tubing connecting the two tubes is of course removed. The limbs of the first tube are closed with bungs until the contents are titrated. The distillation is re-started and continued for a few minutes, after which the second tube is disconnected from the condenser and thistle-funnel and its limbs are closed with bungs.

The contents of the two tubes are transferred to a beaker, and the tubes and glass tubing are rinsed with water, the rinsings being collected in the beaker. Ten ml. of 10 per cent. barium chloride solution and 0·5 ml. of phenolphthalein solution are added, and the liquid is titrated with $N/10$ hydrochloric acid. This figure is subtracted from the equivalent of acid to sodium hydroxide found by titrating in presence of barium chloride in a similar manner. A blank on the apparatus is performed with distilled water in place of the carbonate and the above figure corrected. We have found this blank to be fairly constant and equivalent to 1·8 mg. of carbon dioxide. This part of the process differs from that of Macara[2] in the use of barium chloride and sodium hydroxide in place of barium hydroxide.

BAKING POWDER AND SELF-RAISING FLOUR.—About 0·3 g. of baking powder (or 4 to 5* g. of self-raising flour) and 0·5 g. of tannic acid are weighed on a filter-paper, which is wrapped up and introduced into the flask containing 5 ml. of liquid paraffin and a little pumice. Sixty ml. of water (or 100 ml. if flour is under examination) are run in from the separating funnel, and the determination of water-freed carbon dioxide is made as described above. The acid-freed carbon dioxide may be determined by adding to the residue in the distillation flask 40 ml. of water containing 5 ml. of 10 per cent. phosphoric acid and making a further distillation. The blank result obtained with ordinary flour was found to be the same as that obtained without the flour. The liquid paraffin and tannic acid prevent excessive frothing, the distillation is quite satisfactory, and the method is both accurate and expeditious; the determination of carbon dioxide in sodium carbonate takes about half-an-hour. A known amount of sodium carbonate was added to plain flour (3 g.), and a good recovery of carbon dioxide was obtained (*cf.* No. 7).

A few typical results are set out below:

SODIUM CARBONATE

	CO_2 present mg.	CO_2 found mg.
(1)	4·15	4·1
(2)	4·15	3·9
(3)	20·75	20·7
(4)	41·5	41·0
(5)	62·2	62·0
(6)	124·0†	126·0
(7)	3 g. plain flour +20·75 mg. of CO_2	20·2

BAKING POWDER

	Taken	‡Available CO_2		Total CO_2		
	g.	mg.	Per Cent.	mg.	Per Cent.	
(8)	0·3	29·0	9·7	33·0	11·0	Duplicate determinations
	0·3	31·0	10·3	34·0	11·3	

---

* Less than 5 g. should be taken, as with more than that amount there is a tendency for a very thick paste to be formed towards the end of the distillation, and the flask is liable to crack. The water must be increased if more than 5 g. are used.

† Ten ml. of N NaOH in the first tube; 5 ml. of N NaOH are sufficient for 60 mg. of CO_2 or less.

‡ The CO_2 liberated from aqueous solution on heating.

SELF-RAISING FLOUR

	Taken	Available CO_2		Total CO_2		
	g.	mg.	Per Cent.	mg.	Per Cent.	
(9)	5·0	25·7	0·5	—	—	Triplicate determinations
	5·0	24·0	0·48	31·0	0·62	
	4·0	17·6	0·44	26·0	0·65	

In conclusion we may add that the apparatus here described has been found very useful in the determination of hydrocyanic acid in viscera.

E. T. ILLING
E. G. WHITTLE

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1. E. T. Illing and E. G. Whittle, ANALYST, 1939, **64**, 329.
2. T. Macara, *id.*, 1904, **29**, 152.

COUNTY LABORATORY
COUNTY HALL
TAUNTON
May, 1939

NESSLER CYLINDERS OF LEAD GLASS: A WARNING

IN connection with some work carried out recently on the determination of small quantities of lead in foodstuffs I found that the amounts apparently present were far in excess of those anticipated. Eventually it was discovered that the Nessler cylinders being used were made of lead glass. In view of the fact that the 1914 British Pharmacopoeia (p. 497) states specifically that all Nessler cylinders used for the determination of lead shall be made from lead-free glass, and that the 1932 Pharmacopoeia (p. 549) mentions that all glass used for the determination of lead shall be free from soluble lead, analysts may be pardoned for expecting reputable suppliers to have noted this. I find, in fact, that Nessler cylinders in my possession over 5 years old are free from lead, but that recent deliveries are made of lead glass and I have written this note in the hope that it may catch the eye of analysts and prevent any serious mistakes.

T. McLACHLAN

10A, FEATHERSTONE BUILDINGS
HIGH HOLBORN
LONDON, W.C.1

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF BRISTOL

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1938

OF the 2139 samples examined, 1573 were purchased informally.

WATER IN COOKING FATS.—Two of ten samples contained 8·9 and 7 per cent. of water, respectively. Since cooking fats are generally used as lard substitutes, one would expect them to contain no water. These two samples, however, were sold with a label that they contained "far less moisture than butter or margarine." As this statement was true, the declaration of water would appear to render the sale legal, and no action was taken.

COPPER AND TIN IN TOMATOES.—The copper in 21 port samples of tomatoes and tomato products was determined by the diethyl-dithiocarbamate method after wet ashing; tin was also determined in 15 samples. The following results were obtained:

Description	Total Solids Per Cent.	Copper, p.p.m. in original	Copper, p.p.m. on dried total solids	Tin Grains per lb.
Canned tomatoes	5·32	2·0	37	0·22
,, ,,	5·62	1·1	19	0·36
,, ,,	7·07	0·9	12	0·24
Tomato purée	12·49	3·5	28	—
Canned tomatoes	6·05	3·0	50	0·24
,, peeled plum tomatoes	—	1·95	—	0·045
,, ,, ,, ,, (blown)	—	2·3	—	0·22
,, tomato purée	—	3·7	—	0·66
,, plum tomatoes	—	4·8	—	0·29
,, ,, ,,	—	1·4	—	0·31
Tomato purée	11·18	12	107	0·84
Peeled tomatoes	5·08	2·3	45·7	0·8
Canned peeled tomatoes	5·1	6	117	0·31
,, ,, ,,	5·07	3	60	0·22
,, tomatoes	5·06	1·6	31	0·13
,, ,,	5·36	1·0	19	0·26
Tomato purée	13·3	4	30	—
Canned tomato purée	10·25	10	97·5	—
,, plum tomatoes	5·98	2·2	37·1	—
,, tomatoes	6·03	1·6	26·5	—
,, ,,	5·78	2·0	34·6	—

The amount of copper in tomatoes which was recommended as a provisional limit at a Conference of Port Medical Officers of Health in January, 1938, is 50 parts per million calculated on the dried total solids, and it will be seen from the above table that this amount was exceeded in four samples.

A whole tomato, grown by a member of the staff, contained 1·8 p.p.m. of copper; it had never been sprayed.

ARSENIC IN SALT CODFISH.—A port sample having an objectionable odour of decomposition, and with red patches on the flesh, was examined. The stained portions contained 3 p.p.m. of arsenic, and since the normal amount of arsenic in codfish is about 0·5 p.p.m., the patches of red were apparently related to arsenical contamination. The fish was adjudged unfit for consumption.

MOISTURE IN BARLEY MEAL.—Five samples of barley meal contained from 7·35 to 12·2 per cent. of moisture, whilst another sample, which had been taken at the mill within 48 hours after milling and had been processed by washing, contained 14·1 per cent. Experiments were made to ascertain the moisture-content of 5 samples of barley meal after being freed from moisture and exposed for about six or seven weeks under different conditions. The samples, dried to constant weight at 100° C., were exposed in flat dishes to the air of the laboratory and the weights were recorded every day for 40 days. During that time the relative humidity of the air reached 100 per cent. on at least five occasions. The samples were then exposed to extreme conditions for 10 days, being placed near a ventilator, while air saturated with aqueous vapour was continuously passed over them. Finally, the samples were allowed to remain for six months exposed to the air of the laboratory with a good draught from the open window and door. The results of these experiments were as follows:

	Russian	Russian and Canadian	Persian	Canadian and Persian	Persian
(1) Original moisture, per cent. ..	12·0	12·4	7·35	14·1	10·3
(2) After exposure for 40 days:					
Minimum, per cent. ..	6·8	6·6	7·0	6·65	6·6
Maximum, ,, ,, ..	9·6	9·6	9·95	9·5	9·5
(3) After exposure to air saturated with aqueous vapour:					
Minimum, per cent. ..	9·7	10·5	10·5	9·3	9·5
Maximum ,, ,, ..	13·8	13·5	14·55	12·7	12·9
(4) After exposure for 6 months:					
Minimum, per cent. ..	9·6	8·3	9·7	7·3	8·1
Maximum, ,, ,, ..	11·0	9·8	11·2	8·8	9·7

In these experiments the moisture in the sample which originally contained 14·1 per cent. never reached anything approaching that figure again, whatever the conditions of humidity and time of exposure. It appears therefore that barley meal stored under ordinary conditions might be expected to contain up to 10 per cent. of moisture, and that under extreme conditions, unlikely to occur, the moisture-content might reach 15 per cent. Hence 12 to 13 per cent. would be a perfectly fair maximum limit for the moisture-content of barley meal, and some such limit might with advantage be incorporated in the Fertilisers and Feeding Stuffs regulations.

WATER FROM THE HOTWELLS SPRING.—Two samples of water from this historic well were taken, one at low tide and the other at high tide. The analytical results (parts per 100,000) of the two samples were very similar:

Total solids	100·0	Silica	1·9
Mineral matter	88·5	Iron and alumina ..	0·7
Loss on ignition	11·5	Lime	20·5
Chlorine, as chlorides	7·0	Magnesia..	4·5
Total oxidised nitrogen ..	0·55	Sulphate (SO_3)	27·8
Nitrites	nil	Sodium oxide	10·7
Free ammonia	0·0006	Chlorine	7·0
Albuminoid ammonia	0·001		
Total hardness (Clark's scale) ..	35°	Carbon dioxide	5·4
Permanent hardness (Clark's scale)	19°		
*p*H	7·2	Nitrate (NO_3)	2·5
		Mineral matter ..	81·0

The water has not changed in mineral character to any great extent since the analysis of 15 years ago. Although the chemical figures were satisfactory, the water was not considered suitable for drinking purposes until the bacteriological results were greatly improved.

EFFECT OF CHROMIC ACID ON BRICK, CONCRETE AND SALT-GLAZED PIPES.—The effect of a 3 per cent. solution of chromic acid, the trade effluent from an anodising bath, was investigated. It was found that when this effluent was allowed to act on the sewer materials for four hours at the ordinary temperature, the concrete lost about 11 per cent. in weight and the earthenware pipe only about 0·5 per cent.; brick was also but little affected. Neutralisation of the effluent by the addition of 8 to 10 lbs. of lime per 100 galls. rendered it innocuous.

F. E. NEEDS

COUNTY OF LANCASTER

Annual Report of the County Analyst for the Year 1938

Of the 5157 samples of foods and drugs examined, 1853 were purchased informally.

Drought and the Composition of Milk.—Towards the end of May the newspapers spoke of a possible increase in the price of milk—an increase which would be "the direct result of the drought." Evidence was given before the Departmental Committee, set up by the Board of Agriculture in 1900, to the effect that a period of drought tends to raise the percentage of fat and decrease the solids-not-fat, and Bull. No. 16 (Ministry of Agriculture) states that the quality of milk is depressed by *summer* drought.

A comparison has been made between the average figures for the composition of milk received from the Administrative County of Lancaster during the dry period (February 13th to May 11th—88 days) and the rainfall in inches recorded near Preston during the same period from 1928 to 1938. The number of samples each year ranged from 766 to 927. A table shows that the average figure for fat (3·65 per cent.) for the dry period of the year 1938 (with rainfall 2·74 inches) is the same as in the corresponding period of the year 1929 (with rainfall 3·61 inches). Similarly in 1930 (with rainfall 4·97 inches) the average fat-content is 3·72 per cent., as compared with 3·70 per cent. in 1937 (with rainfall 8·84 inches). For solids-not-fat the 1938 figure (8·74 per cent.) is the same as that for 1935 (with rainfall 7·92 inches). The differences for fat and solids-not-fat in the dry period from the average figures for the eleven years are only slight (0·05 and 0·09 per cent., respectively) and cannot be regarded as significant. The frequencies for fat and for solids-not-fat, together with the rainfall for the dry period, during the eleven years have also been tabulated. These tables have been kindly examined by Dr. A. T. Dodson, F.R.S., Associate Director of the Liverpool Observatory and Tidal Institute, and he concludes that there is no correlation between the frequencies for fat and the rainfall, and the frequencies for solids-not-fat and the rainfall; in other words, that there is no evidence of any influence due to drought on the amount of fat or of solids-not-fat.

Phosphorised Quinine Tablets.—A sample consisted of discs with a gelatin basis, containing, in each tablet, 1/20 grain of quinine sulphate and phosphate equivalent to 2·7 minims of the dilute phosphoric acid of the B.P. 1932. The directions on the label were: "Take two, three times a day." In this quantity a person would take, in the whole day, about one-third of the minimum single dose of quinine. The amount of phosphoric acid would be about half the minimum B.P. dose. As there is no standard fixed for the amounts of quinine and phosphoric acid in phosphorised quinine tablets, the article was reluctantly passed as genuine.

Poisoning by Arsine.—An unusual case was received from the Ormskirk Coroner. A man had been employed for over twenty years as a general labourer in a zinc-white works, and for the past eight months had been working on the zinc-dissolving plant, supplying hydrochloric acid in buckets to the dissolvers. For two years previously the deceased had been in poor health, complaining of pains in the stomach and chest, but after resting he had seemed to recover and then resumed work. The post-mortem report was to the effect that the cheeks and nose were of a bright pink colour, and that the bladder contained a small quantity of blood-stained urine. These are indications of poisoning by arsine, which might have been derived from the interaction of the commercial zinc and the hydrochloric acid, both of which may contain arsenic as an impurity.

The following amounts of arsenic were found in the organs of the deceased:

	As_4O_6 in whole organ mg.	As_4O_6 per 100 g. of organ mg.
Liver	4·10	0·24
Kidneys	1·47	0·35
Lungs	0·63	0·13
Bowels	0·25	0·03
Stomach	0·15	0·05
Spleen	0·14	0·15
Bladder	0·09	0·06
Pancreas	0·05	0·05
Duodenum	0·05	0·02
Hair	0·03	(equiv. to 32 p.p.m.)
Toe, thumb and finger nails	0·17	(equiv. to 60 p.p.m.)
Total	7·13	

As was to be expected, the greatest amount of arsenic was found in the liver, but the greatest concentration was in the kidneys. The amount of arsenic found in the hair (32 p.p.m.) indicated that the intake of arsenic had been going on for some time—probably months at least. The amount found in the nails also supported this conclusion.

Silica in Lungs of a Moulding-shed Worker.—The lungs of a man who had worked in a moulding shed were received from a County Coroner. The pathologist had observed a certain amount of fibrosis of the lungs, and it was thought that, owing to the man's occupation, he might have inhaled siliceous material. The right lung contained 0·90 per cent. and the left lung 0·89 per cent. of silica calculated on the dry tissue.

Abortefacient Pills.—Two pills were submitted in connection with a case of an alleged attempt to procure abortion. They were machine-made and had a white coating consisting principally of talc. Each pill, after removal of the coating, weighed about 4 grains and contained colocynth pulp, aloes and oil of cloves.

Cattle and Polluted Water.—A sample of ditch water was submitted because it was suspected that it might be unfit for cattle to drink. Chemical analysis indicated considerable pollution with organic matter of animal origin. There is a sharp division of opinion among veterinary experts as to the possibility of injury to cattle being caused by the presence of sewage in their drinking water. The *Veterinary Record* for February 10th, 1934, contains a very exhaustive symposium on this subject, and the majority of authorities who contributed took the view that considerable amounts of crude sewage might be present in the drinking water of cattle without causing deleterious results. Indeed, one expert expressed the view that cows might eat freshly-cut grass wet with sewage and escape injury. In view of these opinions it did not appear likely that cattle, drinking water polluted to the extent indicated by the analysis of the sample, would suffer any deleterious effects.

J. R. Stubbs

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

VI. CARBON BISULPHIDE VAPOUR

PROPERTIES.—Carbon bisulphide has b.p. 46° C. and flash-point about 20° C. Its vapour ignites spontaneously at 125°–135° C., so that contact even with a warm steam pipe, or electric lamp bulb, may be sufficient to cause ignition. The minimum explosive concentration in air is 1 part in 50 parts by vol. of air (63 mg. per litre) (Factory Form, 836).

OCCURRENCE.—Dangerous concentrations may be encountered in works in which are manufactured artificial silk (viscose), chemicals, coal gas, vulcanised and "dipped" rubber goods, tar distillation products, etc.

POISONOUS EFFECTS.—The following particulars are based chiefly on the *Toxicity of Industrial Organic Solvents* (H.M. Stationery Office, 1937):—In high concentrations carbon bisulphide may cause delirium, coma and death from respiratory failure. The better-known effects are severe chronic poisoning of the nervous system with a great variety of symptoms, varying in degree from slight fatigue and giddiness to serious mental derangement, blindness and paralysis. The effects of known concentrations in the air are as follows:

Parts by vol. (approx.)	Mg. per litre (approx.)	Effects
1 in 300 to 1 in 500	10 to 6	Serious illness and danger of mania and coma in about half-an-hour.
1 in 3000	1	Severe headache and mental dullness or confusion usually result from an isolated exposure of a few hours' duration. If the exposures are of daily occurrence, the symptoms become increasingly severe, with neuritis, distorted vision and mental disturbance.
1 in 15,000 to 1 in 30,000	0·2 to 0·1	Repeated daily exposures to these low concentrations produce a general condition of ill-health with headache, drowsiness and hysterical outbursts.

These observations show that the permissible concentration of carbon bisulphide vapour in the atmosphere of workrooms should be kept well below 1 part in 30,000 of air (0·1 mg. per litre) and preferably not above 1 part in 100,000 (0·03 mg. per litre).

METHOD OF DETECTION.—The standard method adopted is based on the reaction of carbon bisulphide with diethylamine and copper acetate, producing copper diethyldithiocarbamate. Samples of the air under examination are drawn, by means of a hand-pump of definite capacity, through a bubbler containing the reagents, and the mixture is allowed to stand. The colour developed is compared with a series of standards prepared by adding small quantities of the reagents to dilute alcoholic solutions of carbon bisulphide of known strength. From the number of pump strokes made and the colour obtained, the concentration of the carbon bisulphide is found by reference to a table.

Apparatus.—The method of sampling the air, the arrangement of the bubbler, and the type of pump are described and illustrated (*cf.* ANALYST, 1938, **63**, 659; 1939, 279).

Preparation of Reagent.—(*a*) Two ml. of diethylamine are dissolved in 100 ml. of benzene; (*b*) 0·1 g. of copper acetate is warmed with a little absolute alcohol, and the solution is made up to 100 ml. with absolute alcohol. All the reagents must be of reagent quality.

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* Leaflet No. 6. H.M. Stationery Office, July, 1939. Price 3d. net.

For the test, 10 ml. of absolute alcohol are measured into the bubbler, 2 ml. of solution (*a*) and 2 ml. of solution (*b*) are added, and the mixture is stirred.

Preparation of Standard Colours.—One ml. of carbon bisulphide (reagent quality) is made up to 100 ml. with absolute alcohol, giving a 1 per cent. solution. One ml. of this solution is then made up to 50 ml. with absolute alcohol, giving a 0·02 per cent. solution. The following quantities of the 0·02 per cent. solution are made up to 10 ml. with absolute alcohol, 2 ml. of the diethylamine solution and 2 ml. of the copper acetate solution are added and well mixed, and the mixture is allowed to stand for 15 minutes for full development of the colour. The following standards are thus obtained:

	Standard			
	No. 1	No. 2	No. 3	No. 4
Vol. of 0·02 per cent. carbon bisulphide, ml.	0·02	0·5	1·0	2·0

These standards must be freshly prepared immediately before the test, or at least on the same day. They must be in tubes of exactly the same size as the bubbler. When not in use they must be well corked, or sealed, and kept in the dark.

Application of Test.—Fourteen ml. of the mixed diethylamine and copper acetate reagent are placed in the side-arm test-tube of the apparatus, and the tube is connected with the pump, the valves of which have previously been tested. If traces of hydrogen sulphide are present, a dry lead acetate paper is fixed in a paper holder (such as that used for other tests in this series; *cf.* ANALYST, 1937, **62**, 608), in such a way that the atmosphere entering the solution passes through the lead acetate paper first. (To prepare the lead acetate papers, strips of Whatman No. 1 filter-paper are immersed in a solution obtained by dissolving 10 g. of lead acetate in 100 ml. of water and adding 5 ml. of glacial acetic acid; the papers are then left to dry.)

Pumping of the atmosphere to be tested is carried out with 1, 2, 3, 5 or 20 strokes of the pump (approximately 10 seconds per stroke). The bubbler is then removed and allowed to stand for 15 minutes, after which the depth of colour developed (if any) is compared with the standard colours, the bubbler and the tubes containing the standards being observed side by side in transversely transmitted daylight. Other methods of comparing the colours may be used, such as by means of a comparator using coloured glasses as standard, a photo-electric colorimeter or an optical density meter.

The concentration of carbon bisulphide corresponding with the depth of colour and the number of strokes made, is then read from the following table:—

Number of strokes	Standard No. 1	No. 2	No. 3	No. 4
1	1/6000	1/3000	1/1500	1/750
2	1/12,000	1/6000	1/3000	1/1500
3	1/18,000	1/9000	1/4500	1/2300
5	1/30,000	1/15,000	1/7500	1/3800
20	1/120,000	1/60,000	1/30,000	1/15,000

Where a test is required on air from a space that is not readily accessible, or where there is a possibility of a highly toxic concentration of carbon bisulphide vapour being present, the atmosphere should be sampled from a distance. In the procedure described for this purpose the apparatus is connected with the space to be tested by means of glass tubing (approx. 0·25 in. bore), with rubber connections.

First Aid.—The need for first aid rarely arises except in cases of acute poisoning. If breathing has ceased, or is very weak, artificial respiration may be required. Maniacal symptoms may require control. It should also be borne in mind that on recovery from the comatose condition, the patient may become maniacal.

REPORT OF THE BUILDING RESEARCH BOARD FOR THE YEAR 1938*

THE Report contains an introductory section by the Chairman of the Board, Sir Raymond Unwin, and the Report of the Director, Dr. R. E. Stradling.

Over 3100 enquiries and special investigations were dealt with at the Building Research Station during the year. These included the testing of the suitability of clay from South Wales for making roofing tiles, tests with copper damp courses, tests on the fire resistance of structures, and the examination of two new types of floor—one consisting of a varnish blended with sand, finely divided fillers, and pigment, the other a new type of resiliant rubber floor—and tests on a new type of aluminium glazing bar. Among the investigations reviewed in detail are the following:

ARTIFICIAL POZZOLANAS.—For very many years it has been a common practice in many European countries to use mixtures of Portland cement and certain natural earths for making concrete exposed to chemical attack, or to soil containing sulphates, or to sea water. These earths are known as pozzolanas because the Romans used similar volcanic dust from the region of Pozzuoli in their mortars. There are no natural pozzolanas in this country, but as a result of a long investigation which has now been satisfactorily completed at the Building Research Station, it has been shown that first-rate materials of this nature, equal to the best imported materials, can be produced artificially by burning certain clays at a controlled temperature and by selection from the spent material arising in the Scottish shale-oil industry. The materials are now being produced commercially, and the methods used are also being applied in the manufacture of special bricks from shale-oil material for the Scottish market.

CLEANING OF BUILDINGS.—Samples of the hard, compact incrustation from the face of the keystone and of the loosely adherent deposit beneath the window arch of an old building of Portland stone have been analysed, with the following percentage results:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	CO_2	H_2O and carbonaceous matter (diff.)
Dense incrustation ..	7·25	2·17	1·60	26·90	37·80	0·02	0·38	23·88
Loose deposit ..	8·95	2·71	2·22	24·80	35·50	0·01	0·21	25·60

Both samples gave positive reactions for tar acids and tar bases. The analyses show that they consist essentially of calcium sulphate mixed with dust and soot.

Further successful trials have been made with a new spray process for cleaning buildings, and it has been used in particular for cleaning the Admiralty screen in Whitehall and the Central Telegraph Office. The advantages claimed are that carvings can be completely cleaned however intricate the design, that delicate surfaces can be cleaned without causing the slightest damage, and that the work is so easy as to avoid any temptation to use alkaline detergents or other harmful chemicals for reducing the labour involved.

There are disadvantages. Local authorities raise objection if water is allowed to run over the pavements in busy thoroughfares, and there is some risk of spoiling internal decorations through water penetration. Simple precautions can be taken to minimise these inconveniences. Unlike steam-cleaning or hand-scrubbing with water, the method would doubtless be awkward to operate from cradles; scaffolding is more convenient.

Certain brown stains, not peculiar to this process, due to the effect of tars, which developed particularly on the Admiralty screen, disappear in time.

DAMP PENETRATION OF BRICKWORK.—A small rain machine, constructed for laboratory work, enables one square foot of brick wall to be exposed to a 30 mile per hour wind accompanied by artificial rain of any desired intensity. Tests have been made with this machine on a series of panels in an exposure wall at the Station, and when storms of sufficient severity occur the wetness at the backs of the panels will be compared with that observed in the tests with the rain machine. In the tests some panels were penetrated in about forty minutes, others remained dry at the back after four hours' treatment, but no definite conclusions could be drawn from the tests on the relative merits of the bricks and mortars used in the wall. It is proposed to build a limited number of panels specially for testing with the rain machine, paying particular attention to the effect of faults in workmanship.

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* H.M. Stationery Office, June, 1939. Price 3s. 6d. net.

CHEMICAL STABILITY OF FIRED CLAYS.—Eight clays, each fired at a standard rate to three different temperatures between 850° and 1150° C., have been examined. Measurements have been made of the loss on ignition (at 600° C.) of powdered samples that had been stored in the laboratory, and of the loss on ignition after boiling with water for 6 to 8 hours and after autoclaving for 21 hours at 165° to 170° C. Measurements of the absorption of methylene blue have also been made on the same series of samples. Boiling with water usually increased the dye absorption; samples that had been wetted and dried fifty times showed a higher dye absorption than the corresponding laboratory-stored samples. With few exceptions the loss on ignition and the dye absorption decreased with increase in the firing temperature, but no relationship could be traced between these two properties. Presumably the phenomena are connected in some way with rehydration or hydrolysis of compounds in the fired clay; the chemical reactions involved still require investigation.

THE CORROSION OF CONCRETE.—New work to be undertaken includes an investigation, in co-operation with the Institution of Civil Engineers, on the corrosion of concrete products in various soils. A series of specimens is to be exposed for periods up to ten years at selected sites. After withdrawal of the samples at certain periods and examination in the laboratory it is hoped that recommendations can be issued for avoiding corrosion troubles.

CRYSTALLISATION OF SALTS IN BRICK AND STONE.—It is well known that porous building materials may be completely disintegrated by the hydration of such salts as sodium sulphate within their pores. To investigate the cause of this, a series of experiments has been made in which a porous body (a compressed mixture of sand with the hydrated salt), itself of negligible tensile strength, was subjected to the crystallisation process when carrying known loads. The general results show that when the anhydrous salt (sodium sulphate or magnesium sulphate), or its lower hydrate, becomes hydrated within the pores, it will expand even against pressures greater than the tensile strength of normal porous building materials, irrespective of whether the salt-crystals are completely unrestrained in some directions. Further work is in progress on the diffusion of salts within the pores and on the effect of pore size distribution on the deterioration caused by the crystallisation of salts.

CALCIUM SULPHATE PLASTER.—Among the problems investigated was that of the "burning" of plaster-board during drying in manufacture, causing failure of adhesion of the paper to the plaster. A rapid method was devised for the detection of the dehydration products of gypsum on a set plaster surface similar to that of plaster board. A microscopical method utilising the difference in refractive index between gypsum and its dehydration products has been evolved and appears practicable. Other problems investigated include the penetration of paint on plaster, the mechanism of the adhesion of paint, and the relationship between the porosity and hardness of calcium sulphate plasters.

The other sections of the Report are concerned with structures and strength of materials, with the efficiency of buildings from the standpoint of the user, and with an account of special investigations.

New Zealand

ANNUAL REPORT OF THE DOMINION LABORATORY

THE Seventy-first Annual Report (for 1937) is again drawn up by the Acting Dominion Analyst (Mr. R. L. Andrew, F.I.C.). The work of the year, which consisted almost entirely of analyses and investigations for various Government Departments, involved the examination of 15,452 samples, of which 12,704 were for the Health Department.

MILK.—*The Reductase Test.*—The legal minimum requirement for this test is three hours, but the percentage of samples causing reduction in five hours or under was only 3·4, as in the previous year (*cf.* ANALYST, 1938, **63**, 602). The modified test of the English Ministry of Health, has been found to have distinct advantages and will be substituted for the present test under the New Zealand Sale of Food and Drugs Act.

Phosphatase Test.—The use of this test has been continued in the main laboratory and in three branch laboratories, and its great value has been definitely established. Sometimes pasteurised milk is not labelled, as required by regulation, and customers are supplied with raw or pasteurised milk indiscriminately. The phosphatase test has provided a means of checking this practice. The test has also been used to control the milk supplied in all the larger towns of Canterbury and Westland.

CERATIUM IN WATER SUPPLIES.—A special investigation was carried out on the water of Lake Pupuke from which Takapuna draws its supplies. The presence of the organism *Ceratium* had caused serious trouble in 1934, as it imparts a most objectionable odour and taste to water. When the organism re-appeared in 1937 a special study was made of its life history. It was found that in cool weather the cysts of the organism are very resistant to copper sulphate. Accordingly the copper sulphate treatment of the lake was carried out after microscopic examination of samples of the water from selected points had shown no cysts to be present. The treatment was completely successful, as it was in 1934. The same species of *Ceratium* was found in the sea-water of Auckland Harbour, and, as Lake Pupuke is separated from the sea by a very narrow strip of land, it would appear that the cysts are carried over from the sea.

COMPOSITION OF TOOTHPASTES.—An examination of various brands of toothpaste on the market was made, 31 samples in all being analysed. No abrasive was found in any of the samples, although in much of the advertising it is inferred that rival brands contain abrasives, *e.g.* pumice powder. One brand contained a considerable proportion of potassium chlorate and would be dangerous if used continually. It was recommended that the sale of this paste be prohibited. Two other pastes contained undesirable amounts of iodides.

The most objectionable feature was the extravagant and misleading advertising matter which accompanied many of the samples. There appears to be no necessity for so many different brands, as with one exception the toothpastes appeared to provide simply an agreeable but somewhat expensive method of applying precipitated chalk to the teeth. One of the pastes was acid in reaction, but this would have no advantage over a simple acid wash.

"CANCER CURES."—Samples of preparations on public sale by herbalists were examined. One of the cures consisted of lead powder and another of camphor and "herbs." Action was taken which led to a modification of the claims made for such remedies, but the legal provisions for safeguarding the public in this respect appear inadequate.

ARSENICAL-SPRAY INJURY.—In view of injury to apples after being sprayed with arsenate, an investigation was conducted to ascertain the effect of the "Spreader" Agral II and also of certain hard waters upon the soluble-arsenic figure. The results showed that Agral II caused no increase in soluble arsenic, but that the use of a hard water in the making-up of the arsenate spray gave rise to a dangerously high figure—in one experiment 3·1 per cent. calculated on the dry material. In these instances it was found that the addition of hydrated lime at the concentration of 3 lb. per 100 galls. reduced the soluble arsenic to within a safe figure.

POISONING BY ABSORPTION OF CARBOLIC ACID THROUGH THE SKIN.—In a case in which liquefied carbolic acid, instead of a dilute solution, had been accidently used as a dressing for neuritis in the arm, death resulted from the absorption of the poison through the skin. Traces of phenol were recovered from the liver of the victim.

ALCOHOL IN THE BLOOD AND URINE.—Several specimens of blood and urine were submitted in connection with motor accidents, etc. In three cases significant amounts of alcohol were found; in one case it was in the form of methylated spirit.

IDENTIFICATION OF RABBIT-FUR.—In a case in which a very large number of rabbit-skins had been stolen by night from a warehouse, considerable assistance was rendered to the police by the identification of a number of hair fibres obtained from the clothing of a suspect and from a car which was proved to have been hired by the suspect on the night of the crime. The fibres were proved to be rabbit-fur by microscopical examination, especially of the transverse sections, which are very characteristic.

DECIPHERING FILED-OFF NUMBERS.—The etching method of developing numbers filed off stolen metal articles (*cf.* ANALYST, 1938, **63**, 602) has been continued with success.

Government of Bengal

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1937

THIS is the Sixty-third Annual Report on the work of the Chemical Department and has been drawn up by the Chemical Examiner, Dr. K. N. Bagchi, F.I.C. During the year under review 10,436 articles were examined, as compared with 7747 in the previous year, the increase being mainly due to the transfer of the Bengal Excise Laboratory to the Department. In addition to the routine work several special investigations were carried out, notably two under the auspices of the Indian Research Association—one on arsenic and lead in normal human tissues, and the other on cyanogenetic glycosides in the linseed plant (*vide infra*).

HUMAN POISONING CASES.—The total number of specimens of viscera examined, including 33 in connection with abortion cases, was 870, as compared with 878 in 1936. As usual, the most common poison detected was opium, which was found in 171 articles (37·9 per cent. of the detected poisons). Next, in order of frequency, came alcohol, oleander, arsenic, aconite, copper sulphate, hydrocyanic acid and its salts, and atropine.

Poisoning by Skin Absorption of Paranitroaniline.—The viscera, stomach contents and urine of a man, about 35 years of age, were submitted by the Calcutta Coroner, together with a packet of yellow powder. The deceased was working with other coolies on a steamship until noon. At 1 p.m. he and another coolie were found sleeping on a mat with their bodies covered with a yellow powder. They then returned to work, but at about 5 p.m. complained of feeling giddy and fell down unconscious. They were removed to hospital where one died, whilst the other recovered. It was ascertained by the police that these two coolies had rubbed each other's head, face and body with a yellow powder in the same way as they usually do with red dyes during the "holi" festival. The steamer carried this cargo of yellow dyestuff from France for certain cotton-mills in Cawnpore.

In the post-mortem examination the liver, stomach and other organs were found to be healthy. The kidneys were only slightly congested and the bladder contained some yellow urine. No yellow pigment and no poisonous substance was found in the stomach contents, but a small quantity of yellow pigment was isolated from the urine. This gave some of the reactions of an aniline dye (the quantity was too small for full analysis) and resembled the dyestuff which had been handled by the coolies. This yellow dyestuff, which melted at 147° C. (after recrystallisation), was found to be paranitroaniline. It had a toxic action on frogs, rats and cats, killing them in a short time. It was readily absorbed through the unbroken skin, and, as a 20 per cent. ointment with vaseline, killed a frog in 30 minutes and a cat in about 6 hours when applied to the abdominal wall. Further work on the toxicology of this dyestuff is in progress.

Marking-nut Poisoning.—Garments were sent for the identification of marking-nut oil (*Semecarpus anacardium*), which had been poured by a jealous woman on to the genitals of another woman while she was asleep (*cf.* ANALYST, 1936, **61**, 614). The case was submitted under Sec. 32, I.P.C. ("causing grievous hurt").

CATTLE POISONING.—The viscera of 122 horned cattle were examined, and poison was detected in 82 of the specimens; arsenic was found in 75, oleander in 5, and a cyanogenetic glycoside in the remaining 2.

Oduvan as Cattle Poison.—A semi-solid substance was sent from Bargarh in connection with a case of an attempt to poison cattle. The specimen consisted of finely-divided roots and leaves of *Cleisanthus collinus* (oduvan), made into a paste and mixed with straw. It was thrown in front of a cow grazing in a field. Oduvan has frequently been used for homicidal purposes, and as a fish poison, but its use for poisoning cattle has not previously been recorded. (*Cf.* ANALYST, 1936, **61**, 613.)

Chopped Human Hair as Cattle Poison.—In the course of a fortnight exhibits were received from three different districts in connection with cattle poisoning. The preparation of one poisoner included hair and coarsely powdered bone, that of the second contained hair and an inert earthy substance, and the third contained hair and lime. It is interesting to note that these cattle poisoners, living far apart and speaking different languages, obviously believed in the efficacy of human hair as a cattle poison, but so far there is no evidence that chopped hair actually kills cattle.

Use of Caustic Soda to Disable Buffaloes.—An irritant substance, submitted from Bagerhat, had been applied to the necks of buffaloes, and had caused intense inflammation and ulceration. On analysis the substance was found to consist of caustic soda with traces of carbonates. This is a novel form of disabling buffaloes. The object appears to be to harm the owner rather than to kill the animal for the sake of its hide, which is the usual motive of professional cattle-poisoners.

NORMAL LEAD-CONTENT OF HUMAN TISSUES.—An investigation, published in detail elsewhere (*cf.* p. 698) gave results differing considerably from those recorded by European and American workers, so that the European or American Standard cannot reasonably be applied to Indian cases.

TOXICOLOGY OF LINSEED PLANT.—Cattle poisoning by linseed flowers is fairly common in Bengal and Bihar. The results of an investigation on the subject have been completed and published (K. N. Bagchi and H. D. Ganguli, *Indian J. Vet. Science*, 1939, **9**, 61–66). The amounts of hydrocyanic acid liberated by the enzyme linase, from different parts of the plant, were determined: (i) in distilled water, (ii) in 0·4 per cent. hydrochloric acid, and (iii) in 0·4 per cent. sodium hydroxide solution. In each test the plant was ground up and kept in the medium (water, acid or alkali) for about 4 hours at room temperature before the determination. The following results were obtained:

Part of plant	Hydrogen cyanide liberated in water Per Cent.	hydrochloric acid Per Cent.	sodium hydroxide solution Per Cent.
Roots	0·067	—	—
Leaves	trace	trace	nil
Stems (only the tops taken after removal of flowers)	0·128	—	—
Flowers before fertilisation	0·08	—	—
Flowers after fertilisation (*i.e.* with immature seeds)	0·69	0·6	0·16
Mature fruits (ready for harvesting)	0·08	0·05	0·02
Linseed	0·06	0·04	0·01
Husks or bolls (after removal of seeds), used as fodder	0·05	0·04	0·01

The linseed flowers with immature seeds may therefore be regarded as the most potent cattle poisons. About half-a-pound of these flowers is sufficient to kill a bullock. Very dilute acids or alkalis only retard the action of the enzyme, but *N* acid or alkali inhibits the action. A strong solution of an alkali (sodium carbonate) has been suggested for use as an antidote in linseed flower poisoning. The possibility of poisoning by hydrocyanic acid should always be borne in mind in investigating obscure cases of cattle poisoning.

British Standards Institution

THE following new British Standard Specification has been issued*:

No. 756—1939. APPARATUS FOR THE DETERMINATION OF WATER BY DISTILLATION WITH AN IMMISCIBLE LIQUID.

This Specification replaces two earlier ones, namely, B.S. No. 614, "Graduated Receivers for Dean and Stark Apparatus," and B.S. No. 756, "Apparatus for the Determination of Small Quantities of Water by Distillation with an Immiscible Liquid."

Whilst retaining, with only minor modifications, the less expensive receivers of B.S. 614, the present Specification includes also receivers with identical graduated portions but fitted with ground-glass joints. The size of the joint adopted for the receivers is the same as in B.S. 756. The side-arm of each receiver ends in a cone of a ground-glass joint, size No. B.24 of B.S. 572, so that the receivers can be used only with boiling-flasks having the appropriate socket of a ground-glass joint of that size.

Two types of apparatus are provided for in the Specification. Type 1 is based on the Dean and Stark apparatus, and Type 2 is an apparatus that the Fuel Research Station has found well suited for the determination of water in coal and coke. To meet various requirements, four sizes of receiver have been specified for Type 1 apparatus.

In preparing this Specification the Committee made use of the paper by Tate and Warren (ANALYST, 1936, **61**, 367), and reference to that paper is recommended for details of procedure and choice of immiscible liquids.

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* Publications Department, 28, Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Artificial Colouring of Egg Yolk by the Addition of Sudan Dyes to Poultry Food. A. Asshof. (*Z. Unters. Lebensm.*, 1939, **77**, 578–579.)—The natural pigments lutein, zeaxanthin, carotene and ovoflavin are not synthesised in the organism of the hen but are derived from food, especially green food of high vitamin-content. It has recently been the practice in the poultry-food industry to induce a deep colour in egg yolk by addition of fat-soluble synthetic dyes to the food. Grossfeld and Kanitz (*Z. Unters. Lebensm.*, 1935, **69**, 582; Abst., ANALYST, 1935, **60**, 700) regard this addition as an adulteration, because the artificial dyes differ in chemical composition from the natural pigments, and especially because they suggest the presence of valuable accessory food substances, which are, in fact, not present to the extent indicated by the colour. Feeding experiments were made upon a group of hens, 100 mg. of "Sudan red B, specially pure," dissolved in 2 ml. of arachis oil being administered to each hen per day before the first meal of corn and green food. Under the influence of the dye the laying power diminished, rapidly at first and then more slowly until, after 46 days, the hens stopped laying. All the birds lost weight visibly and two died. The whole of the body fat of the dead birds was of an unnatural dark red colour and they were obviously unfit for use as food. The dye appeared in the outer layer of the yolk on the third day after the first administration and, in the eggs laid subsequently, the colour deepened and spread towards the centre. Eggs laid 13 or 14 days after the experiments had been discontinued contained no detectable dye. When 19 eggs containing the dye were incubated in an electric incubator, 10 showed no development, and in the remaining 9 the embryo had ceased to develop after 12 to 48 hours. In a control series of 20 eggs laid after the experiments had been discontinued and containing no dye only 2 showed no development, 3 contained dead embryos which had developed for 10 to 15 days, and in the remaining 15 the embryos were alive and normally developed. Inclusion of the dye in poultry-food therefore destroys the germinating power of the egg and affects both the laying power and the general health of the hen. The amount of dye, estimated by comparison with standard solutions, was 0·1 to 0·3 mg. per egg, and, although this amount may be considered too small to affect human health adversely, the practice must, for reasons already stated, be regarded as an adulteration. A. O. J.

Detection of Fluorides in Wines, Beers, Jams and Fruit Jellies, and in Butters and Margarines. G. Destrée. (*J. Pharm. Belg.*, 1939, **21**, 501–504, 527–530.)—*Wines.*—Existing methods for the detection of fluorides by the etching method are criticised. Thus a preliminary precipitation as barium fluoride may give low results owing to the solubility of the precipitate, and high results because of adsorption of insoluble barium compounds (*e.g.* barium sulphate), especially with wines having a high alcohol-content. The solubility of calcium fluoride is less than that of barium fluoride, but it is high enough to introduce an error when the quantity of fluoride in question is less than 2 mg. Disadvantages attached to the formation of calcium fluoride by neutralisation with lime water followed by evaporation and calcination, are that the quantities of lime water necessary are often large (especially with wines), and contribute silica to the ash, and that the subsequent addition of sulphuric acid to the slightly alkaline ash produces heat and effervescence, with consequent loss of hydrofluoric acid. Errors due to the action of hydrofluoric acid in the glass containing-vessels cannot be disregarded. These difficulties are overcome by the following method, which involves precipitation as lanthanum trifluoride (*cf.* Meyer and Schulz, ANALYST, 1925, **50**, 637). To 5 ml. of wine are added 2 ml. of a solution containing 10 per cent. of ammonium acetate and 5 per cent. of acetic acid, and 3 ml. of a 2·5 per cent. solution of lanthanum acetate. The mixture is shaken well during the following hour, and filtered 11 hours later, and the vessel and filter are washed with two 5-ml. portions of a solution containing 5 per cent. of ammonium acetate and 2·5 per cent. of acetic acid. The filter and its contents are then ignited at dull red heat in a platinum dish (height 4 cm. and diameter 3·5 cm.), which is afterwards completely covered with a rubber disc in the centre of which is a hole (diameter 2·5 cm.). Through this is introduced 0·5 ml. of conc. sulphuric acid, and the dish is at once covered with a piece of ordinary window-glass, the lower side of which has been coated with a thin layer of carnauba wax, on which have been written (with the back of the nib of a pen) some letters, 0·25 cm. high. The glass plate is held in position by means of a moistened wad of wool placed on its top surface, and in contact with this is placed a suitable cooling device. The crucible is then cautiously heated until the fingers can no longer be placed on its hottest portion. The burner is withdrawn for 15 minutes, after which heating is continued, with a small flame 10 cm. under the crucible, for 45 minutes. In this way a sharp legible etching was obtained with 5 ml. of a 100 per cent. dilution of a red, a white, and a liqueur wine, each of which contained 10 mg. of fluoride ion per litre. When the quantity of wine used, or the fluoride-content, was halved, a lens was necessary to read the etched writing, but only a legible etching was regarded as a positive result. If the fluorine is present as a fluosilicate instead of as an alkaline fluoride, the following modified method is preferable, although not always essential:—The wine is first boiled with sodium carbonate (which converts the fluorine into sodium fluoride), and then boiled with ammonium zincate solution until all the ammonia has been driven off; the silica (as zinc silicate) and the excess of zinc (as hydroxide) can then be removed by filtration. The solution is then diluted to the original volume of the wine taken (*e.g.* 5 ml.), 2 drops of a saturated solution of disodium hydrogen phosphate are added, and the fluoride is precipitated with lanthanum acetate as described above. Legible etchings were obtained with 5 ml. of wine containing 0·025 mg. of fluoride ion, but not with 2·5 ml. of such wine. *Beers.*—The precipitation is carried out as already described, except that 2 drops of a saturated solution of disodium hydrogen phosphate are also added in order to precipitate lanthanum phosphate, which carries down the lanthanum fluoride if this is present only in small quantities. The subsequent procedure is also the same as already described, the lanthanum phosphate being insoluble in the dilute acetic acid used in the wash-liquor. The limiting sensitiveness of the test is then 0·025 mg.

of fluoride in 5 ml. of beer. *Jams and Fruit Jellies.*—In presence of much citric acid precipitation of the fluorides is incomplete, owing to the formation of lanthanum citrate, which is soluble in presence of excess of lanthanum acetate or a citrate; this precipitate is more soluble in the cold than in the warm solution. The following modified method is therefore recommended:—A mixture of 10 g. of the sample, 4 ml. of the ammonium acetate and acetic acid solution, and 5 ml. of the lanthanum acetate solution is boiled, and 3 drops of the disodium hydrogen phosphate solution are added. The mixture is shaken at intervals for 1 hour and allowed to stand for 11 hours, after which 20 ml. of water are added, the mixture is again boiled and filtered while hot, and the precipitate is washed twice with 5-ml. portions of the warm wash liquor (see above). In this way a legible etching was obtained with 10 g. of a sample (equivalent to about 4 g. of fruit or fruit juice) containing 0·05 mg. of fluoride. The modifications described are unnecessary if tartaric acid is present and citric acid is absent. *Butters and Margarines.*—The fat is separated by heating gently 100 g. of the sample, and the casein and albuminoids in 5 ml. of the aqueous layer are precipitated with 0·5 ml. of a 50 per cent. solution of trichloro-acetic acid. The solution is boiled, and 4 ml. of the ammonium acetate and acetic acid mixture are added to the boiling liquid, followed by 3 ml. of the lanthanum reagent and 2 drops of the disodium hydrogen phosphate solution. The remainder of the procedure is the same as that described for the original method, except that if the sample is salted the precipitate should be washed until all chloride is removed. Legible etchings were obtained with 5 ml. of the aqueous portions of samples containing 0·2, 0·1 and 0·05 mg. of fluoride ion. It is pointed out that, since any sodium fluoride present in a fatty food dissolves in the water present, the addition of 0·5 mg. of fluoride ion to 100 g. of a sample containing 15 per cent. of water would produce a concentration of fluoride in the water of 3·3 mg. per 100 g. J. G.

Iodimetric Determination of Acidity in Wines. P. Vièles. (*Bull. Soc. Chim.*, 1939, **6**, 1127–1129.)—The reaction used is expressed by the formula $IO_3' + 5I' + 6H^{\cdot} \rightarrow 3I_2 + 3H_2O$. Five ml. of wine and 5 ml. of 0·2 *N* "iodo-acidimetric" solution standardised on iodine (7·6 g. of KIO_3, 50 g. of KI and 49·6 g. of $Na_2S_2O_3.5H_2O$ per litre) are shaken together in a small flask (12 to 15 ml.) and diluted with freshly-boiled water, and the flask is stoppered and left at room temperature for 24 hours. With new wines carbon dioxide is previously expelled. The mixture is poured into a wide-bottomed precipitation vessel, the flask is rinsed out with 5 ml. of water followed by 5 ml. of starch paste, and the liquid is titrated with 0·05 *N* iodine solution. The colour of the mixture does not interfere with the end-point, which should, however, be read at once, as reducing substances present in the wine will affect it within a minute. Results obtained by this method are slightly higher than those given by the French official method, using litmus paper, *e.g.* 5·91 as against 5·81. D. G. H.

Determination of Oenotannin. E. Negre. (*Ann. Falsif.*, **1939**, **32**, 175–178.)—For the determination of oenotannin (wine tannins) as distinct from non-tannin polyphenols, various methods have been investigated, notably the conditions affecting precipitation by means of ammoniacal zinc acetate solutions.

For fairly wide limits of alkalinity the quantity of gallotannin precipitated varies but little, but the range of alkalinity within which zinc gallate is precipitated is small. The zone of complete precipitation of gallotannin overlaps with high degrees of alkalinity that of non-precipitation of gallic acid. Curves were plotted for white and red wines to which known quantities of gallic acid or gallotannin had been added, and not only was it found possible to determine these quantities, but the curve for wine to which no gallic acid had been added was of the same general form as that of a mixture of gallotannin and gallic acid, showing a maximum and a level stretch. This latter appeared to correspond with the total precipitation of oenotannin, and with that only. On treating the wine with ammoniacal zinc acetate solution under conditions of alkalinity corresponding with the level stretch of the curve, and redissolving the precipitate in acidulated water, this solution (but not the treated wine) gave a precipitate on addition of a gelatin solution; but both the treated wine and the solution gave a green colour with iron alum, showing the presence of polyphenols. It is not possible to separate the colouring matters of wines in this way. The method adopted for the precipitation of the oenotannin was to add 10 ml. of reagent (40 g. of zinc acetate, 110 ml. of 22° Bé. ammonium hydroxide solution, made up to 1 litre) for 10 ml. of wine, previously neutralised with ammonium hydroxide, to separate and wash the precipitate rapidly by centrifuging, and to determine the tannin by means of a 0·1 *N* solution of potassium permanganate in the presence of indigo carmine. D. G. H.

Tunisian Olive Oils and Fitelson's Reaction for the Detection of Tea-seed Oil. R. Marcille. (*Ann. Falsif.*, 1939, **32**, 172–175.)—Fitelson's method for the detection of tea-seed oil in olive oils (*J. Assoc., Off. Agr. Chem.*, 1936, **19**, 493; Abst., ANALYST, 1936, **61**, 771) has been studied. The reaction may be made quantitative by following the original directions, but cooling the 10 ml. of ether in ice-water, and then, after mixing the reagents and oil, allowing 4 minutes' contact, and finally immersing the tube in ice-water. Under these conditions the colour develops more slowly, attaining its maximum intensity after 45 minutes and remaining stable for 5 minutes. Comparison may be made, against a background of white paper, with tubes containing potassium permanganate solution, since it has been found that 10 per cent. of tea-seed oil gives a colour very close to that of 0·1 ml. of a 0·1 *N* potassium permanganate solution in 100 ml. of water, and that 20 per cent. corresponds with 0·225 ml. of the permanganate in 100 ml. of solution. On applying the reaction to samples of olive oil of different origin it was found that authentic samples from Tébourba and Ghardinaou in northern Tunisia showed more or less pronounced colour reactions, although all other samples gave negative results. Hence before concluding an olive oil to be adulterated with 10 to 15 per cent. of tea-seed oil, the source of the oil should be ascertained. It is hardly likely that Tunisian oils are the only varieties that give the colour. D. G. H.

Tannic Acid Gauze. R. M. Savage and W. P. Chambers. (*Pharm. J.*, 1939, **143**, 105–107.)—The term "tannic acid" here denotes the pharmacopoeial material, and "gallotannin" that part of the crude product precipitated by an alkaloid in the analytical process, so that tannic acid is regarded as consisting mainly of gallotannin, with gallic acid, water and other impurities. It was found possible in using Mitchell's process for the determination of gallic acid (ANALYST, 1923, **48**, 2) to match the tints of the solutions, without dilution, in the Lovibond tintometer, and from a graph it is seen that with pure solutions of gallic acid the relation between red colour and concentration is nearly linear; a table is given of results with known quantities of gallic acid added to tannic acids of various origins. A plus correction of 15 per cent. should be made for adsorption error. With gallotannin Mitchell's reagent gives a colour similar to, but not identical with that obtained with gallic acid; with some difficulty the former can be matched in Nessler glasses against gallic acid colours, and a factor used for conversion to gallotannin. In comparing tannic acid gauzes and plain gauzes moistened with tannic acid, the dried gauzes were soaked in water and the expressed liquid was analysed. About half the tannic acid was found in the extract from 7½ per cent. gauzes; by analysing tannic acid solutions before and after gauze had been soaked in them about 45 per cent. was found to be adsorbed after 5 minutes, and the result was not very different after 33 minutes. Adsorption is an inevitable result of the use of any form of the compress method. The proportion of the total of tannic acid found in the extract increases with the concentration, and the proportion of the total gallic acid in the extract decreases as concentration rises, the gallic acid being less strongly adsorbed than gallotannin. This relative rise takes place if plain gauze is immersed in fresh tannic acid solution. Although in most instances no hydrolysis appeared to occur in gauzes of various strengths stored for 2 years, yet the weakest gauze stored in a packet showed a higher ratio of gallic acid to gallotannin than a control in a glass jar. Thus it is possible that a small amount of deterioration may take place in 2 years, but the packet specimen actually yielded more of the active agent—gallotannin—than the other. In the analysis of gauze for total tannic acid, extraction with 40 per cent. acetone was found the most satisfactory method, but the results were on the average about 15 per cent. high, the standard error being 6·3 per cent. Although no antiseptic is necessary to prevent mould growth, it may be required for therapeutic purposes. Even slowly volatile substances are unsuitable, but antiseptic mercuric chloride seems possible, as is also euflavine, and, at a high dilution (1 in 20,000), phenylmercuric nitrate. Sterilisation of tannic acid gauze in an autoclave causes some hydrolysis, but about 80 per cent. of the gallotannin originally present is left. D. G. H.

Rapid Colorimetric Assay for Belladonna and Stramonium including their Preparations. N. L. Allport and E. S. Wilson. (*Pharm. J.*, 1939, **143**, 100–102.)—The method used is based on Morin's modification of Vitali's colour test for solanaceous alkaloids (*J. Pharm. Chim.*, 1936, **23**, 546; Abst., ANALYST, 1936, **61**, 504) adapted to make it quantitative. To 1 g. of Belladonna Leaf or Root, as No. 60 powder, are added 1 ml. of 95 per cent. alcohol and 0·1 ml. of 10 per cent. w/w ammonium hydroxide and, after mixing, about 5 ml. of chloroform. The mixture is heated to boiling, and the drug is transferred to a dry miniature percolator (17·5 cm. long by 8 mm. in diameter sharply narrowed about 3 cm. from one end), plugged with about 0·2 g. of cotton-wool and suspended in a stoppered 100-ml. measuring cylinder. Extraction with chloroform is continued until the volume of percolate is 31 ml., and then sufficient 6 per cent. acetic acid (made by dilution with approximately 5 per cent. alcohol) is added to bring the level of the liquid to the 80-ml. mark, after which the cylinder is stoppered, gently shaken for 25 seconds, and allowed to stand. When the upper layer is free from coloured chloroform about 5 ml. of this layer are pipetted off and filtered, and 1 ml. of the filtrate is evaporated to dryness on a water-bath. The residue is treated at once with 0·2 ml. of fuming nitric acid (sp.gr. 1·5, analytical reagent quality) and the dish is left on the boiling water-bath for 3 minutes, after which the residue is dissolved in 3 ml. of acetone, and the solution is transferred to a 10-ml. measuring cylinder by means of acetone, cooled and made up to 10 ml. with acetone. Then 0·1 ml. of a 3 per cent. solution of potassium hydroxide (reagent quality) in methyl alcohol (prepared not more than a fortnight previously) is added, and the cylinder is stoppered, inverted once, and left for exactly 5 minutes. The resulting colour is matched immediately in a Lovibond tintometer, and the value for the red component is correlated with the amount of alkaloid present by means of a graph or by reference to the following table, and calculated by the appropriate factor into percentage of alkaloid as hyoscyamine in the original sample.

Hyoscyamine mg.	Colour after dilution to 10 ml.; observed in 1-cm. cell, Lovibond units		
	Red	Blue*	Brightness*
0·025	1·2	0·8	0·2
0·05	2·6	1·8	0·6
0·07	4·0	2·4	0·7
0·075	4·3	2·6	0·8
0·10	6·2	3·5	1·0
0·125	8·4	4·3	1·2
0·135	9·1	4·5	1·5
0·15	10·6	5·4	2·1

* These values are subject to slight variations. They are included as guides to accurate matching, but only the values for the red component are considered in the calculation of results. As the colour produced is brighter than that of the Lovibond glasses, it is necessary to subdue it by means of the neutral tints.

Stramonium leaf is treated in the same way, but 2 ml. of filtered solution of alkaloid in acetic acid are used. Powdered Belladonna Leaf, B.P., is mixed with 0·5 g. of sawdust previously extracted with ether and passed through a 60-mesh sieve. One ml. of 95 per cent. alcohol and 0·1 ml. of dilute ammonia solution are added, and the percolation with chloroform is continued as for Belladonna Leaf. With Tinctures of Belladonna and Stramonium, 15 ml. are evaporated to about 5 ml., 2 ml. of 95 per cent. alcohol are added, and evaporation is continued down to 1 ml.; 1 g. of sawdust and 0·1 ml. of dilute ammonia solution are then added, and the assay is completed by percolation with chloroform. With Liniment of Belladonna, B.P., and Chloroform of Belladonna, B.P.C., 1 ml. is used, and 0·1 ml. of dilute ammonia solution, and 0·5 g. of sawdust are added. For Liquid Extract of Belladonna, 0·5 ml. of extract, 0·5 ml. of alcohol, 0·5 g. of sawdust and 0·1 ml. of ammonia solution are used; for Extract of Stramonium, B.P.C., 2 ml. of extract, 0·1 ml. of dilute ammonia solution, and 1 g. of sawdust are used; for Glycerin of Belladonna, B.P.C., 1 g. with 1 ml. of 50 per cent. alcohol, 0·1 ml. of dilute ammonia solution, and 1 g. of sawdust are used, and for Green Extract of Belladonna, B.P.C., and Extract of Stramonium, the same procedure is followed, but 0·5 g. of the sample and 0·5 g. of sawdust are used. For Dry Extract of Belladonna, B.P., 0·5 g. is treated with 1 ml. of 50 per cent. alcohol and, after warming and stirring, with 0·1 ml. of dilute ammonia solution, and 0·5 g. of sawdust are mixed in with a rod; for Dry Extract of Stramonium, 0·5 g. is treated with 0·5 g. of lard, 1 ml. of 50 per cent. alcohol and 1 ml. of chloroform, followed, after warming, by 0·1 ml. of dilute ammonia solution and 0·5 g. of sawdust. Ointment of Belladonna, B.P.C., is treated as the dry extract, 1 g. with 1 ml. of 50 per cent. alcohol and 1 ml. of chloroform being used. The maximum discrepancies were ± 4 per cent. of the actual alkaloid present. The assay for belladonna root and leaf takes about ¾ hour, tinctures rather longer, and such preparations as liniment and liquid extracts half-an-hour. The colorimetric method is not applicable to *Hyocyamus niger* or its preparations, or to plaster and collodion of belladonna.

D. G. H.

Alkaloids of different Species of Senecio. R. Konovalova and A. Orekhov. (*J. Ob. Chem.*, 1938, **8**, 391; *Pharm. Weekblad*, 1939, **76**, 1029.)—The authors' work on the *Senecio* alkaloids supplements that of Van der Meer (*Pharm. Weekblad*, 1938, **75**, 1169; Abst., ANALYST, 1939, 51). It has been found that the senecionine from *S. vulgaris* (common groundsel) is decomposed on hydrolysis into senecionic acid, $C_{10}H_{14}O_4$, and retronecine ($C_{18}H_{13}NO_2$), an amino-glycol. The latter can be reduced to $C_{18}H_{13}NO$, which on dehydration yields an unsaturated base, $C_{18}H_{11}N$, identical with heliotridine. On hydrogenation of this base a compound $C_{18}H_{15}N$, identical with heliotridane, is formed. *Senecio platyphyllus* and *S. stenocephalus* yield seneciphylline, which is decomposed by hydrolysis into seneciphyllic acid, $C_{11}H_{14}O_5$ and the amino-glycol retronecine. The alkaloids of all the species of *Senecio* examined contain the same heterocyclic nucleus: $C_{18}H_{15}N$.

Vanillin and Hydrochloric Acid Reaction for Yohimbine. J. A. Sánchez. (*Investig. Anal. Quím. Funcion. Orgánica*, 1938, **3**, 50.)—When 1 mg. of yohimbine is heated in a dry tube with 1 ml. of vanillin reagent (0·5 g. of vanillin in 100 ml. of hydrochloric acid), a rose-violet compound, soluble in water without alteration, is produced. The colour resembles that obtained with morphine and pseudomorpine derivatives, but differs in that this latter colour is discharged by the action of water. The reaction is due to the indole nucleus in yohimbine; pyrolysis of yohimbine with soda-lime yields vapours which, when condensed or dissolved in alcohol, give the reaction with vanillin in hydrochloric acid. E. M. P.

Reaction of Adrenaline with Mercuric Salts and its Application to the Analysis of Medicinal Preparations. P. Bouvet. (*J. Pharm. Chim.*, 1939, **29**, 481–503.)—The colour reaction given by mercuric salts with adrenaline has been investigated. The nature of the precipitate, the influence of acidity and alkalinity, of the concentration of the mercuric ion, and of chlorides and proteins, have all been studied, and the following technique has been evolved:—A suitable quantity of material is extracted with 0·05 *N* sulphuric acid, and to 10 ml. of the extract are added in succession 9 ml. of water, 0·5 ml. of Baudouin and Lewin's nitro-mercuric reagent for the precipitation of proteins (*Bull. Soc. Chim. biol.*, 1927, 9, 302*), and 0·5 ml. of *N* sodium hydroxide solution. After 1 minute the mixture is filtered through an ashless paper. The filtrate is pink and has *p*H about 3. The incipient oxidation (which is indicated by the pink colour) is too slow to interfere with the final determination. Into a test-tube are now poured in the order named, 9·5 ml. of sodium acetate solution (12·5 per cent.), 0·5 ml. of 0·1 *N* sulphuric acid, 2·5 ml. of the filtrate, and 3 drops of mercuric nitrate solution containing 1·5 per cent. of mercury. On shaking, the pink colour at once develops and attains its maximum (permanent) colour after 5 minutes, the *p*H being about 6·9 and the liquid clear. A comparative test should be carried out by treating 0·002 g. of adrenaline, with 10 ml. of 0·2 *N* sulphuric acid, water, nitromercuric reagent and sodium hydroxide as before (2 ml. of filtrate ≡ 0·2 mg. of adrenaline). The method was checked in presence of protein by adding 0·002 g. of adrenaline to 5 g. of a testicular powder and extracting the mixture with 0·2 *N* sulphuric acid; colorimeter readings gave 19·9 and 20·1 as against 20 for the standard. With powdered suprarenal gland the percentage error in four determinations was between +2·5 and −3·4, and with extract of fresh adrenal gland in 5 determinations it was between −3 and +2·2. To determine the adrenaline in the French Codex (1937) Solution, 1/1000, which contains 0·84 g. of chlorine per 100 ml., or about 1·7 mg. in a sample corresponding to 0·2 mg. of adrenaline, the chlorine must first be eliminated. The chlorine is determined by a modification of the Volhard method after destruction of the adrenaline with potassium permanganate and nitric acid on a water-bath in the presence of excess (*n* ml.) of silver nitrate, *e.g.* for 5 ml. of solution 20 ml. of 0·1 *N* silver nitrate solution may be used. Five ml. of adrenaline solution, *n* ml. of 0·1 *N* silver nitrate solution and water up to 50 ml. are mixed and filtered, and for the determination 2 ml. of the filtrate, 9·5 ml. of 12·5 per cent. sodium acetate solution, 0·5 ml. of 0·1 *N* sulphuric acid and 3 drops of mercuric nitrate solution are taken, and the resulting colour is compared after 5 minutes in a colorimeter with a standard containing 2 ml. of 1 per 10,000 solution of adrenaline which has been treated with the other reagents as described above. The adrenaline solution is prepared by dissolving 0·1 g. of adrenaline in 10 ml. of 0·1 *N* sulphuric acid and making up to 1000 ml. with water. A stock solution of 1/1000 may be preserved for several days by adding toluene. The presence of sodium sulphite, up to 0·1 mg., in the sample does not affect the reaction. The error was +2 to −2 per cent. Details are also given for the determination of adrenaline in adrenal extracts for injection, in powders of the gland, and in fresh beef adrenal gland. Results obtained by this method compared with those given by physiological assays showed close agreement. Drying of the adrenal gland had little effect upon the adrenaline-content. D. G. H.

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*BAUDOUIN AND LEWIN'S REAGENT.—Red mercuric oxide (145 g.) is added little by little to 105 ml. of pure nitric acid (sp.gr. 1·383), with constant stirring until solution is nearly complete. One hundred ml. of water are added, and the mixture is heated until a clear solution is obtained. This is cooled and diluted with water to 700 or 800 ml., 35 ml. of *N* sodium hydroxide solution are stirred in gradually, and the liquid is made up to 1 litre and filtered.

Biochemical

Fatty Acid Oxidation in Liver. L. F. Leloir and J. M. Munoz, (*Biochem. J.*, 1939, **33**, 734–746.)—The action of rat-liver slices on normal fatty acids containing 1 to 8 carbon atoms was studied by incubating the tissue slices with different substrates for 2 hours, and withdrawing samples for analysis at the beginning and the end of the incubation. Sodium bicarbonate, acetoacetic acid, β-hydroxybutyric acid and fatty acids were estimated in the solutions, a new technique being devised for the estimation of fatty acids. This comprised, first, the acidimetric titration of the acid isolated by distillation, and, secondly, estimation of acids with 3 to 8 carbon atoms by oxidation with potassium dichromate of the acids isolated by distillation (acetic acid is not oxidised under the conditions employed). *Precipitation of proteins.*—This was carried out in both instances, either by the copper-lime method of Edson (*Biochem. J.*, 1935, **29**, 2082) or, where liver "brei" was used instead of liver slices, by the addition of an equal volume of 10 per cent. zinc sulphate solution and sufficient sodium hydroxide solution to turn the colour of phenol red to orange-yellow. *Acidimetric titration.*—An all-glass electrically heated distillation apparatus was used, and the flask was surrounded by a wide glass tube and the column enclosed in cotton-wool. Six ml. of the deproteinised sample were measured into the flask, followed by 2 g. of anhydrous sodium sulphate and 1 ml. of sulphuric acid (2 volumes of conc. acid to 1 volume of water). The distillation was continued until 5 ml. of distillate had been collected. This was boiled for 10 seconds in presence of a small crystal of barium chloride to remove carbon dioxide and detect the presence of sulphuric acid, which should be absent. The solution was then titrated with 0·01 *N* sodium hydroxide solution, with phenolphthalein as indicator. *Oxidation.*—Interfering substances were first removed by adding 0·2 ml. of 2·5 *N* sodium hydroxide solution, and 0·2 to 0·3 g. of powdered mercuric oxide (yellow) to the deproteinised solution (6 to 8 ml.) and heating the mixture in a boiling salt-bath (105° C.) so that it was kept boiling. After 1 to 2 hours, when the volume had been reduced to half, the tube was allowed to cool, and the contents were transferred to the distillation flask and distilled as described above. The resulting distillate (5 ml.) was then treated with 10 ml. of oxidising mixture (2·45 g. of potassium dichromate were dissolved in 1 litre of conc. sulphuric acid and the solution was heated until white fumes appeared), and the solution was heated in a boiling water-bath for 1 hour. The contents of the tube were then diluted with 100 ml. of water, and 1 ml. of 10 per cent. potassium iodide solution was added. The liberated iodine was titrated with 0·025 *N* sodium thiosulphate solution. A blank with distilled water was treated with oxidising mixture in the same way. *Results.*—In tests with pure solutions 95 per cent. of acetic acid was recovered after distillation, whilst recovery for the other acids was practically quantitative. The results of the dichromate oxidation showed errors not exceeding 10 per cent.

Measurements made by this method of the rate of disappearance of fatty acids from substrates by the action of liver slices gave the following results (expressed in μl* of acid per mg. of tissue per hour): formic 1·5, acetic 5, propionic 2, butyric 9, valeric 2, hexanoic 6, heptanoic 3, and octanoic 6. Oxalic and glycollic acids were shown not to be intermediaries in the disappearance of acetic acid, and it was found that only about 20 per cent. of the latter was converted into ketonic acids, the fate of the remainder being unknown. The rates of disappearance of propionic and valeric acids were so low that no attempt was made to find out how they were oxidised. Butyric acid was the most rapidly oxidised of all the acids tested and 80 to 90 per cent. of it was oxidised in the β-position. Hexanoic and heptanoic acids also appeared to be oxidised in the same way, but octanoic acid was oxidised in two ways, one part giving 2 molecules of ketonic acid and another part 2 molecules of acetic acid and 1 molecule of ketonic acid. F. A. R.

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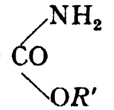
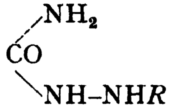
* This unit, the micro-litre, here denotes the quantity of a compound which, if it were in the form of a gas at N.T.P., would occupy one millionth of a litre; 22·4 μl therefore represent one millionth of a gram-molecule of the compound.

New Sensitive Colour Test for Urea. J. A. Sánchez. (*Investig. Anal. Quím. Funcion. Orgánica*, **1938, 3,** 192–195.)—The basis of the test is the formation of a colour when the product of the interaction of urea and phenylhydrazine reacts with vanillin in hydrochloric acid. The procedure is: Five drops of 1·5 per cent. phenylhydrazine hydrochloride solution and 3 drops of urea solution are introduced into a test-tube, which is placed in a glycerin bath at a temperature not exceeding 120° C.; when evaporation from the tube is complete the temperature is raised and maintained between 160° and 170° C. for 5 minutes (not longer). After cooling, 10 drops of a solution of 0·5 g. of vanillin in 100 ml. of pure hydrochloric acid are added, and the tube is immersed in a boiling water-bath for 1 minute (not longer). A more or less intense currant-red colour then appears. The reaction seems to be typical of the carbamide group  $\mathrm{CO}\begin{smallmatrix}\nearrow \mathrm{NH_2}\\ \searrow \mathrm{O}R'\end{smallmatrix}$, since it is obtained when methyl and ethyl urethanes or barbituric acid and some of its derivatives (diethylmalonyl urea) are heated with phenylhydrazine hydrochloride at 160° C. Criogenine and macetine, both of which contain the group  $\mathrm{CO}\begin{smallmatrix}\nearrow \mathrm{NH_2}\\ \searrow \mathrm{NH{-}NH}R\end{smallmatrix}$, give the colour when warmed with the vanillin reagent. E. M. P.

Colour Reaction for Creatine and Creatinine. J. A. Sánchez. (*Investig. Anal. Quím. Funcion. Orgánica*, 1938, **3,** 155.)—About 3 cg. of creatinine are boiled with 2 cg. of mercuric oxide and 2 ml. of water until the oxide is reduced. The liquid is decanted into another tube, about 5 cg. of resorcinol are added, and, when this has dissolved, 2 ml. of pure conc. sulphuric acid (free from nitrites) are run down the side of the tube. The upper layer shows a blue colour which becomes more intense with time. If, after 10 minutes, the contents of the tube are mixed, the entire liquid becomes indigo-blue. The first stage of the reaction is probably the oxidation of creatinine to oxalic acid and methylguanidine, the oxalic acid giving the colour reaction. Creatine is oxidised similarly. E. M. P.

New Colour Reaction of Glycine and Hippuric Acid. J. A. Sánchez. (*Investig. Anal. Quím. Funcion. Orgánica.*, **1938, 3,** 131–134.)—When glycine (0·05 g.) is heated with 10 drops of 1 per cent. permanganate solution in a test-tube over a small flame, with continuous agitation, for 15 seconds, the colour is discharged and a precipitate of manganic oxide appears. One drop of conc. sulphuric acid and 5 cg. of powdered oxalic acid are added, and the tube is shaken until the precipitate has dissolved and the liquid is colourless. The mixture is then treated successively with 3 ml. of 1 per cent. phenylhydrazine hydrochloride solution, 3 drops of 5 per cent. potassium ferricyanide solution, and 30 drops of pure conc. hydrochloric acid, with shaking; an eosin-pink colour appears. Sodium hypochlorite or potassium chromate may be used as the oxidising agent instead of permanganate. With hippuric acid the procedure is: About 0·05 g. of hippuric acid is heated with 1 ml. of water and 2 drops of conc. sulphuric acid until solution is complete. Ten drops of 1 per cent. permanganate solution are added, and the tube is shaken until the manganic oxide is precipitated. Oxalic acid (0·05 g.) is added, the tube is shaken until the precipitate dissolves and the liquid is colourless, and Schryver's test for formaldehyde (ANALYST, 1909, 34, 471) is then applied.

E. M. P.

Action of Barium Hypobromite on Leucine. J. A. Sánchez. (*Investig. Anal. Quím. Funcion. Orgánica*, 1938, 3, 151.)—On adding 1 ml. of barium hypobromite solution to a solution of 0·05 g. of leucine in 2 ml. of hot water and heating, there appears a precipitate consisting of barium carbonate and valeric aldehyde. The barium hypobromite is prepared by adding bromine water to 5 ml. of saturated baryta water until the solution is slightly yellow. E. M. P.

Estimation of Fructose and Glucose in Blood and Urine. R. W. Martin. (*Z. physiol. Chem.*, 1939, 259, 62–74.)—The method proposed utilises the blue colour formed by treatment with diphenylamine and hydrochloric acid to measure the amount of fructose present, *n*-propyl alcohol being employed to produce a clear solution. The protein is removed by means of cadmium hydroxide, and the resulting solution can be used for the estimation of both fructose and glucose. Only 1 ml. of blood is required, and the error involved is about 5 per cent. As soon as possible after removal from the vein, 1 ml. of the blood is added to 8 ml. of cadmium sulphate solution (13 g. of cadmium sulphate dissolved in 63·5 ml. of *N* sulphuric acid and made up to 1 litre) contained in a 30-ml. centrifuge tube. The mixture is shaken, 1 ml. of 1·1 *N* sodium hydroxide solution is added and, after further shaking, the suspension is centrifuged for 5 to 10 minutes. The supernatant liquid is filtered, and 4 ml. of the filtrate (which can be stored at 0° C., if necessary, for 24 hours without loss of reducing power) are transferred to a 50-ml. conical flask and treated with 2 ml. of conc. hydrochloric acid and 0·4 ml. of 10 per cent. alcoholic diphenylamine solution. Some diphenylamine may crystallise out, but this is unimportant. The flask is then fitted with a loosely-fitting stopper and heated in a boiling water-bath for 15 minutes and then cooled in running water for 3 minutes. Four ml. of *n*-propyl alcohol are added, the flask is shaken for 20 minutes, and the colour of the liquid is measured in a Pulfrich step-photometer (filter S 61); for the blank, a solution containing no fructose is treated in the same way. The fructose-content of the blood may be calculated by reference to a calibration curve. Glucose is estimated in 1 ml. of the protein-free filtrate by the method of Fujita (*Biochem. Z.*, 1930, **225**, 368; 1931, **242**, 43), the amount of fructose being subtracted from the amount of reducing substances present.

When urine contains appreciable amounts of fructose, it must first be diluted 10 or 100-fold, so that the solution contains 0·5 mg. in 4 ml., and it is then unnecessary to clarify and decolorise the urine. Otherwise, 10 ml. of the urine are shaken with 2 g. of neutral lead acetate, and the suspension is filtered. The filtrate is treated with 1 ml. of saturated sodium phosphate solution to remove excess of lead, and the resulting solution is used for the estimation, which is carried out in the same way as for blood, distilled water being used for the blank in the measurement of the colour. F. A. R.

Normal Urinary Fluorine Excretion and the Fluorine-content of Food and Water. W. Machle, E. W. Scott and J. Treon. (*Amer. J. Hygiene*, 1939, **29**, 139–145.)—The normal quantity of fluorine excreted by the urine is slightly more than 1 mg. per litre; in a district (Arizona, U.S.A.) where the drinking water has a high fluorine-content and mottling of the enamel of the teeth is endemic, the urinary fluorine excretions greatly exceed those in normal districts, and also appear to be directly correlated with the quantities of fluorine in the drinking water. Where the fluorine-content of the water is low (less than 0·1 mg. per litre) the fluorine in the local foodstuffs accounts for the greater part of the fluorine intake and excretion; the absolute quantity of fluorine ingested with food does not differ greatly in areas of low and high fluorine-contents of the water, but in the latter areas the fluorine contributed by the food is relatively unimportant compared with that contributed by the drinking water. Food plays a small rôle in the production of mottled enamel.

E. M. P.

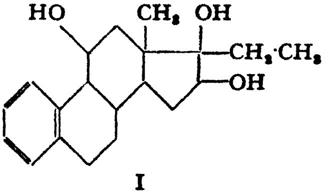
Quantitative Estimation of Porphobilinogen in the Urine of Patients suffering from so-called Acute Porphyria. B. Vahlquist. (*Z. physiol. Chem.*, 1939, **259**, 213–221.)—Porphobilinogen can be purified, according to Waldenström, by chromatographic adsorption of acidified urine on a column of alumina, followed by elution of the appropriate zone with dilute ammonia. The colourless solution of porphobilinogen so obtained is substantially free from other organic substances and condenses with Ehrlich's *p*-dimethylaminobenzaldehyde reagent to give a red product with two absorption bands—a strong one at 570 to 550$m\mu$ and a weaker one at 530 to 515$m\mu$. To estimate porphobilinogen in a pure solution, 4 ml. of the sample are mixed with 4 ml. of the reagent (prepared by dissolving 20 g. of *p*-dimethylaminobenzaldehyde in 500 ml. of conc. hydrochloric acid and diluting to 1 litre), and the mixture is allowed to stand for 1 minute in the 1-cm. or 2-cm. cell of a Pulfrich photometer. The colour is then measured in relation to that of a mixture of 4 ml. of the reagent (which has a slight yellow colour) with 4 ml. of water, filter S 55 being used. From the extinction value so obtained, the number of "porphobilinogen units" is calculated by reference to a calibration curve. With urine the estimation is not so simple, and urobilin, if present (Schlesinger's reaction with iodine), must be removed by extracting the urine with ether after acidifying with acetic acid. The urine is then centrifuged or filtered and its absorption at 550$m\mu$ is measured in the step-photometer. It is then diluted to sp.gr. 1·00025, and the value of the extinction after treatment with the reagent is measured as described above for a purified solution. The reason for diluting the urine is that urea inhibits the formation of the red colour; by diluting to the sp.gr. named, the amount of urea present, and therefore the degree of inhibition, is made approximately constant. The porphobilinogen-content is read from a curve corresponding with 10 per cent. inhibition, after a correction has been made for the absorption of the original urine. F. A. R.

Polarographic Detection of the Biologically important Ketones of the Sterol Group. J. Eisenbrand and H. Picher. (*Z. physiol. Chem.*, 1939, **260**, 83–99.)—A steroid ketone having a double bond conjugated with the keto group usually possesses a greater biological activity than the corresponding saturated ketone. Thus testosterone is 6 to 7 times as active as androsterone, whilst progesterone, corticosterone and desoxycorticosterone all possess high biological activities. The detection of such unsaturated ketones is therefore of more importance than the detection of steroid ketones generally. A method has now been devised that is claimed to have many advantages over the existing colorimetric and spectrophotometric methods. It depends on the reduction of the ketone with a dropping mercury cathode and a mercury anode. The apparatus used had an automatic recording device to indicate the increase or decrease in the current that took place as the voltage was stepped up, the current being measured by means of a mirror galvanometer, the light from which fell on to moving photographic paper. From 1 to 7 mg. of the substance to be tested was dissolved in alcohol and the solution was diluted to 9 ml. One ml. of aqueous *N* lithium chloride solution was added, and the solution was transferred to the electrolytic cell. A stream of oxygen-free nitrogen, washed with 90 per cent. alcohol, was passed through the solution, and the current was measured, as described above, for a voltage range of 1·2 to 2·2 with a sensitivity of 1/15. The resulting tracings showed a well-defined inflexion at 1·6 to 1·8 volt with testosterone, testosterone propionate, progesterone and desoxycorticosterone acetate, whereas androsterone, dehydroandrosterone and dehydroandrosterone acetate, gave curves that were quite smooth. With the same ketone, the height of the inflexion was proportional to the concentration of the substance, so that the method can be used as a basis of assay. With substances that contain more than 100 mg. per 100 g., it is usually possible to estimate the ketone-content directly in 90 per cent. alcoholic solution without preliminary treatment, except that oil solutions are dissolved in 5 volumes of petroleum spirit and extracted several times with 80 per cent. ethyl alcohol. With extracts of tissues, however, which may contain 10 mg. or less per 100 g., a preliminary concentration must be carried out, and for this Girard's reagent "T" is recommended. For instance, 175 ml. of alcoholic testicle extract were dried with potassium carbonate and concentrated under reduced pressure to 40 ml. After the addition of 3·5 ml. of glacial acetic acid and 2·5 g. of reagent "T," the mixture was heated for 1 hour under reflux, allowed to cool and poured on to 150 g. of ice and 40 g. of water, and the mixture was treated with *N* sodium hydroxide solution until just neutral to bromothymol blue. Water was added to reduce the concentration of alcohol to 10 per cent., and the suspension was extracted with seven 50-ml. portions of ether.

The aqueous layer was made up to 500 ml. with 10 per cent. alcohol, and 135 ml. of 3·5 *N* sulphuric acid were added to make the final solution 0·75 *N* acid. After standing for 1 hour at room temperature the suspension was extracted with five 50-ml. portions of ether, and the combined extracts were filtered and dried over potassium carbonate. The residue left after removal of the ether was dissolved in 5 ml. of alcohol, giving a solution nearly 40 times more concentrated than the original; this was used for the polarographic estimation in the usual manner. The height of the inflexion was measured, and the testosterone-content was calculated from the height of the inflexion given by a testosterone solution of known strength. It was found to be equivalent to 1·27 mg. of testosterone per 100 g. of the original testicle extract, corresponding to a biological activity of 84 units per 100 ml. The activity found by biological assay of the same extract was 66 units, the difference between the two results probably being accounted for by the presence of other unsaturated ketones, such as androstendione. The testosterone-content estimated by the spectrophotometric and colorimeter methods showed even greater divergence from the value found by biological assay. F. A. R.

Oxidation of Cholesterol and Trans-Dehydroandrosterone with Osmium Tetroxide. M. I. Ushakov and A. I. Lutenberg. (*J. Ob. Chem.*, 1939, **9**, 69–72.)—In the oxidation of trans-dehydroandrosterone and of cholesterol with osmium tetroxide in ethereal solution there are formed cis-androstan-3, 5, 6-triol-17-one and cis-cholestan-3, 5, 6-triol, respectively, isomeric with the corresponding products which are obtained on hydrolysis of trans-dehydroandrosterone oxide and cholesterol-α-oxide. The triols obtained are characterised by their conversion into the diacetates and by the oxidation of the secondary hydroxyl groups which are attached to C_3 and C_6. Androstan-3, 6, 17-trione was obtained by the reduction of Δ^4-androstene-3, 6, 17-trione with zinc and acetic acid. Details of the methods used are given (*cf.* also Ushakov and Lutenberg, *Nature*, 1937, 466). E. B. D.

Constitution of Cafesterol I. H. Hauptmann and J. França. (*Z. physiol. Chem.*, 1939, **259**, 245–250.)—Slotta and Neisser (*Ber.*, 1938, **71**, 1991, 2342) isolated from the unsaponifiable fraction of coffee-oil, a substance which they called cafesterol and for which they proposed formula I. This structure has now been shown to be inconsistent with the chemical properties of the substance, and it is suggested that formula II represents the probable constitution. The position of the two additonal double bonds is not yet certain.



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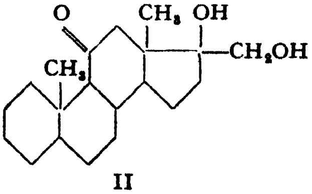

II

F. A. R.

Varying Activity of Vitamin A Concentrates prepared from Fish-liver Oils. T. Moll and A. Reid. (*Z. physiol. Chem.*, 1939, 260, 9–42.)—In 1934 a solution of β-carotene in coconut oil was selected as the international standard preparation for the biological assay of vitamin A, one international unit being defined as the activity of 0·6γ of β-carotene. As a supplementary method of assay, the measurement of the extinction coefficient $E^{1\%}_{1\,\mathrm{cm.}}$ at 328*m*μ was sanctioned, with the use of a factor 1600 for converting the value of $E^{1\%}_{1\,\mathrm{cm.}}$ into international units. Attention is now directed by the authors to the inconsistency of using "a physical property that carotene does not possess, for calculating activity in international units which are defined in terms of carotene," when evidence is available that vitamin A and β-carotene are not of equal biological value. Vogan, a commercial concentrate of vitamin A, contains the vitamin in its natural esterified form. This has been assayed biologically, together with a number of other vitamin A concentrates, by a method (devised by the authors) that is claimed to be independent of the international standard preparation, and the results of which are expressed in biological "rat units." A "rat unit" is defined as the daily dose of substance that is required to produce a weight increase of at least 15 g. in 5 weeks *and* to prevent xerophthalmia. In carrying out an assay, graded doses are given to groups of at least 10 rats, and the daily dose that just gives the requisite growth-increase in all the rats is taken to indicate the weight of 1 "rat unit." By assaying the standard preparation of β-carotene in this way, the relationship between international units and "rat units" was found to be approximately 3:1. This factor has been used to calculate the biological activities of various preparations which are recorded in the following table. This also includes the Carr–Price values and values of $E^{1\%}_{1\,\mathrm{cm.}}$ 328*m*μ, and the factors required to convert the latter into international units.

Preparation	Carr–Price value	$E^{1\%}_{1\,\mathrm{cm.}}$ 328*m*μ	Biological activity (I.U./g.)	Conversion factor
Vogan 3062	2000	34	120,000	3500
,, ,, saponified ..	2000	34	60,000	1800
,, 3065	2000	33	120,000	3600
,, 2977	2000	32	120,000	3700
"Standard Oil II"	16	0·4	1300	3300
U.S.P. Reference C.L.O. ..	80	1·44	2400	1900

On the basis of these assays, it is claimed that the conversion factor for natural esterified vitamin A is about 3500, although for the free alcohol it has the value fixed by the International Commission, namely, 1600. The authors believe that natural esterified vitamin A has twice the biological activity of vitamin A in the free state. F. A. R.

Reducing Action of Ascorbic Acid on Mercuric Chloride. R. Indovina and F. Manfroi. (*Gazz. Chim. Ital.*, 1939, 69, 117–121.)—Ascorbic acid reduces mercuric chloride to mercurous chloride according to the equation

$$2HgCl_2 + C_6H_8O_6 = C_6H_6O_6 + Hg_2Cl_2 + 2HCl.$$

The reaction is quantitative, as was found by weighing the quantity of mercurous chloride produced by causing varying quantities of ascorbic acid and mercuric chloride to react. The velocity of the reaction was studied by determining the specific conductivity of the solution after different times; the conductivity of the mercuric chloride solution is sufficiently small to be negligible in comparison with that of the hydrochloric acid produced. The reaction is one of the few known examples of a trimolecular reaction. E. M. P.

Absorption Spectra of the Compounds formed by Androsterone and Testosterone in the *m*-Dinitrobenzene Reaction. G. O. Langstroth and N. B. Talbot. (*J. Biol. Chem.*, 1939, **128**, 759–774.)—Attempts to devise a colorimetric method of estimating androgens by means of their reaction with *m*-dinitrobenzene in presence of alkali have not so far been very successful. The difficulties of the method are that other substances interfere and that no distinction is made between the various hormones, which differ markedly in biological activity. An investigation of the absorption spectra produced in the *m*-dinitrobenzene reaction by synthetic androsterone and testosterone was therefore undertaken with a view to effecting improvements in the colorimetric method. A measured quantity of a solution of androsterone or of testosterone, or of both, in absolute alcohol, was diluted to 0·20 ml. by the addition of alcohol, and 0·20 ml. of an absolute alcoholic solution of *m*-dinitrobenzene (11·6 mg. per ml.) was added, followed by 0·20 ml. of a 2·5 *N* absolute alcoholic potassium hydroxide solution. The mixture, together with a blank containing no hormone, was placed in a constant-temperature bath at 25·1° ± 0·1° C., and the colour was allowed to develop for the desired length of time (usually 80 minutes). The mixtures were then diluted to an appropriate volume with absolute alcohol and transferred to absorption cells for spectroscopic examination, which was completed within 15 minutes of dilution. A Spekker photometer and a Hilger E2 quartz spectograph were used. The absorption curve of the reaction mixture obtained from androsterone had a maximum at 520*mμ* and a minimum at 380*mμ*; that from testosterone had a maximum at 380*mμ* with low absorption at 520*mμ*, but with increasing absorption towards the short wave-lengths. The shapes of the curves were altered somewhat by varying the conditions of the reaction, especially with testosterone. The shape of the curve obtained with mixtures of the two hormones was almost identical with that calculated by superimposing the individual curves on one another, but the values of the extinction were lower than the calculated values. This has been shown to be due to a decrease in the amount of the androsterone compound formed in the presence of testosterone. Allowance is made for this phenomenon in the following empirical formulae:

$$M = 1{\cdot}10 - (1{\cdot}20 + 0{\cdot}174\ \mathrm{K}_{380} - 0{\cdot}316\ \mathrm{K}_{520})^{\frac{1}{2}}$$

$$m = \frac{3{\cdot}52\ \mathrm{K}_{380} - (\mathrm{K}_{520} + 0{\cdot}24)}{13{\cdot}3}$$

where M represents the amount (in mg.) of androsterone, m that of testosterone, K_{380} the observed extinction at 380*mμ*, and K_{520} the observed extinction at 520*mμ*.

The following table indicates the close agreement found between the known values and those calculated from the above equations, and between the biological assay (expressed as equivalent mg. of androsterone) and the "spectrochemical" assay obtained by adding the androsterone content to 6 times the testosterone-content. In the seventh column of the table is given the "sterone" assay, obtained by reading from the calibration curve of androsterone the amount of androsterone that would give an equivalent extinction at 520$m\mu$.

Known composition		Determined composition				
Andro-sterone	Testo-sterone	Andro-sterone	Testo-sterone	Biological assay	Spectro-chemical assay	"Sterone" assay
0·11	0·10	0·12	0·10	0·71	0·72	0·12
0·11	0·30	0·11	0·31	1·91	1·97	0·16
0·15	0·19	0·16	0·20	1·29	1·36	0·17
0·32	0·10	0·39	0·10	0·92	0·99	0·31
0·32	0·21	0·32	0·24	1·58	1·76	0·30
0·22	0·31	0·19	0·34	2·08	2·23	0·22

F. A. R.

Toxicological and Forensic

Lead in Human Tissues. K. N. Bagchi, H. D. Ganguly and J. N. Sirdar. (*Indian J. Med. Res.*, 1939, **26**, 935–945.)—Individual variations in the amount of lead normally present in human tissues are due to differences in the quality and quantity of food ingested. The recorded lead-content of normal tissues of Europeans is much higher than that of Indians, the nature of the diet and the conditions of living in the West being responsible for this difference. In the investigation to ascertain the normal lead-content of the tissues of Indians every possible care was taken to ensure a fairly representative selection. All hospital cases or cases with a terminal illness causing partial starvation, and thereby a disturbed metabolism and an interference with the normal intake of lead, were excluded, and only cases of fatal street accidents, shooting, stabbing, suicidal hanging, etc., were selected. The dithizone method of Lynch, Slater and Osler (ANALYST, 1934, **59**, 787) was used for the determinations, with a slight modification to prevent the formation of a yellow colour which interferes with the colorimetric matching and to eliminate traces of oxidants likely to be present in the solution. This modification consists in treating the oxidation products with ammonium oxalate at two different stages of the analysis as suggested incidentally by the authors of the method. This method provides a satisfactory means of determining lead in all biological materials except bones and teeth. Concordant results of duplicate analyses and the satisfactory recovery of added quantities of lead satisfied the authors as to the accuracy and usefulness of the dithizone method for the purposes of this investigation. The following amounts of lead (mg. per kg. of fresh material) were recorded, the figures in brackets representing the numbers of specimens examined:—Liver (9), min. 0·31, max. 0·82, aver. 0·57; kidney (8), min. 0·37, max. 0·71, aver. 0·50; spleen (5), min. 0·30, max. 0·52, aver. 0·36; stomach (8), min. 0·20, max. 0·60, aver. 0·41; small intestine (6), min. 0·20, max. 0·60, aver. 0·38; large intestine (5), min. 0·30, max. 0·68, aver. 0·55; heart (5), min. 0·45, max. 0·75, aver. 0·56; lungs (5), min. 0·30, max. 0·60, aver. 0·45; blood (6), min. 0·11, max. 0·45, aver. 0·24; thyroid (4), min. 0·40, max. 0·60, aver. 0·48; ovary (6), *nil*; placenta (6), min. 0·30, max. 0·36, aver. 0·32; uterus (5), min. 0·05, max. 0·47, aver. 0·28; testes (4), min. 0·30, max. 0·40, aver. 0·34; brain (5), min. *nil*, max. 0·10, aver. 0·07; muscle (5), min. 0·14, max. 0·70, aver. 0·33; skin (3), min. 0·33, max. 0·50, aver. 0·44; scalp (2), min. 1·0, max. 1·2, aver. 1·1; fat (3), *nil*; cartilage (5), min. 0·45, max. 3·25, aver. 1·58; teeth (6), min. 15·5, max. 23·0, aver. 20·7; hair (88), min. 6, max. 508·0, aver. 80·9; nails (3), min. 11·3, max. 12·7, aver. 12·0. The largest amount of lead is found in hair, especially the black hair of Indian women. The colour of hair appears to be related to its lead-content. The skin, in spite of the fact that histologically it is closely related to hair and contains numerous hairs and hair follicles, is very poor in lead. There is no evidence to support the view that foetal tissues have a special affinity for lead. The highest foetal figures recorded were 1·8 in the liver and 6·0 in long bone of a foetus nine months old. A foetus, five months old, contained 0·28 mg. per kg. in the liver; this foetus was obtained from a healthy pregnant woman who committed suicide by hanging. The necropsy tissues from children yielded low lead figures. The following table shows the maximum amounts of lead (mg. per kg.) found in normal tissues in individuals of different nationalities:

Tissues	Indian, authors' results	American, recorded by Kehoe *et al.*	British, recorded by Tompsett and Anderson
Liver ..	0·82	0·80	4·63
Kidney ..	0·71	0·70	2·60
Heart ..	0·75	trace	—
Lungs ..	0·60	0·30	0·88
Intestines ..	0·68	0·20	—
Spleen ..	0·52	2·60	5·9
Cartilage ..	3·25	—	—
Skin ..	0·50 (skin) 1·20 (scalp)	1·30	—
Brain ..	0·10	0·10	0·72
Bones ..	8·5 (rib) 14·86 (flat)	11·4 (long bone) 11·1 (flat)	12·9 (rib)

The lead-content of the normal tissues of Indians is practically of the same magnitude as recorded by Kehoe, Thalmann and Cholak (*J. Ind. Hyg.* (U.S.A.), 1933, **15**, 271), in connection with two healthy cases, one being a negro. On the other hand the results are much lower than those of Tompsett and Anderson (*Biochem. J.*, 1935, **29**, 1857; Abst., ANALYST, 1935, **60**, 772) on material obtained, not from healthy individuals; but from patients who died in hospital from various illnesses.

Water

Ochres of the Waters of the Liège Ardennes. G. Van Beneden. (*J. Pharm. Belg.*, 1929, **23**, 423–426; 449–451.)—The carbonated ferruginous waters of the Ardennes are bicarbonate waters, which are saturated with carbon dioxide, but astringent from the presence of iron, and when exposed to the air deposit oxy-carbonate of iron. In prospecting for new supplies of ferruginous waters the first indication of the presence of iron is the ochre deposit in the beds of streams, ponds, etc. There are, however, several kinds of so-called ochre deposits. The rightly-named "ochre deposit" consists of iron oxy-carbonate, which effervesces with dilute hydrochloric acid, gives the thiocyanate reaction for ferric iron, and, when suspended in doubly-distilled water, shows a *p*H of about 7·0; it is formed from the water of mineral springs, which has a *p*H of 5·1 to 5·5 rising to about 7·7 after loss of CO_2 and deposition of iron oxy-carbonate. Iron bacteria are rarely encountered in these waters. There is also the ochre-coloured sediment of soft surface waters of the Ardennes, which penetrate the quartzose rocks and form numerous springs. This water is of meteorological origin, and the iron it collects is insoluble and remains in suspension as fine particles which have crumbled from the surface; these particles, however, are present in sufficient quantity to form incrustations and to obstruct pipes. This deposit is almost insoluble in hydrochloric acid, does not affect the *p*H of doubly-distilled water and gives the thiocyanate reaction for ferric iron. Iron bacteria, mostly leptothrix and crenothrix, are frequently found in these deposits; their growth is promoted by the organic matter present in the surface water and, although originally almost colourless, the accumulation of suspended particles in their filaments makes them appear brown. A third type of ochre-like deposit is that formed from the ferruginous waters of the Eupen district. These waters are not carbonated, and the iron is present as ferrous sulphate, the deposit formed on oxidation being basic ferric sulphate. With doubly-distilled water this deposit gives a *p*H of 4·8 to 5·1. It is readily soluble in dilute hydrochloric acid, and the solution gives the thiocyanate reaction for ferric iron. Iron bacteria are not found in it. Fourthly there are the ochre-like deposits formed in the peaty waters of the valleys. These waters are also rich in ferrous sulphate, and when surface waters containing dissolved oxygen flow into them basic ferric sulphate is formed. These peaty waters are very acid. The incrustation of water mains by the various ochre or ochre-like deposits is a serious matter; its prevention and the mode of treatment of the water will of course depend upon the nature of the deposit formed. For the second class of waters described, filtration and sedimentation are all that is required. D. R. W.

Vessel for Sampling Sea-water. E. Pellerin. (*Compt. rend.*, 1939, **208**, 1039–1041.)—The vessel was designed to enable samples of sea-water to be taken at a required depth. It consists of a metal tube to hold about 2½ litres, sufficiently strong to withstand pressures up to 250 m. of water and provided with a screwed-on lid carrying entry tube, air-release tube and a central rod. The open ends of the tubes are closed by an obturator carried down the central rod and held in position against a spring by means of a spring-collar projecting a little from a slot cut around the rod. Above the obturator is a sleeve on the rod with a wide flange, constituting the opening device. The vessel is lowered to the desired depth by a cable attached to the upper end of the rod. To admit the water when required, a heavy ring is allowed to fall down the cable. This knocks down the sleeve, which compresses the collar, allowing the obturator to rise on its spring. When the vessel is full a valve closes the tubes. A pressure gauge is fitted to the vessel for measurement of the water-pressure inside, from which the depth of sampling can be found. The construction throughout is of rustless metal. S. G. C.

Proportion of Zinc in Sea-water. G. Bertrand. (*Compt. rend.*, 1938, **207**, 1137–1141.)—For the determination of zinc in sea water from, *e.g.* the English Channel, a 1-litre sample is evaporated to one-quarter volume in a platinum dish, after the addition of 1 ml. of conc. hydrochloric acid. Sulphate is precipitated with a slight excess of 20 per cent. barium chloride solution (about 35 ml. required). Without filtering, about 12 drops of perhydrol and 40 ml. of conc. ammonia solution (free from carbonate) are added, followed by sufficient of a suspension of calcium carbonate, added little by little, to precipitate the magnesium. [Mediterranean sea water, which is richer in salts, is evaporated to one-third the volume after addition of 2 ml. of hydrochloric acid, and 50 ml. of ammonia instead of 40 ml.] The precipitate is separated by centrifuging, dissolved in the minimum of dilute hydrochloric acid (volume of solution 250 to 300 ml.) and re-precipitated with ammonia and a little calcium carbonate. For the highest accuracy, a second or third re-precipitation may be given. The liquids from the precipitations are combined, the zinc is determined as described by Bertrand, Javillier and Mokragnatz (*id.*, 1906, **142**, 320; *cf.* Bertrand and Javillier, *Bull. Soc. Chim.*, 1908, [IV], **3**, 114; Abst., ANALYST, 1908, **33**, 144) and weighed as zinc sulphate. [The ammonia-calcium carbonate method for the separation of traces of zinc has been previously described, *vide* Bertrand and Mokragnatz, *Bull. Soc. Chim.*, 1923, **33**, 1539).] The following results were obtained:

Origin of sample	Volume of sample (litres)	Zinc, per litre (mg.)
North Sea	2	3·10
English Channel ..	1	3·44
Atlantic	2	3·08
Mediterranean	2	3·79
Dead Sea	0·25	4·37

It was concluded that the amount of zinc bears a fairly constant relationship to the total salts present in sea water, *viz.* about 1:10,000. With Dead Sea water, however, the proportion is considerably less, only about 1 part of zinc to 54,000 parts of total salts. This difference is in favour of the hypothesis that the Dead Sea is not a residue of a former part of the Mediterranean but a lake of much-evaporated Jordan water.

S. G. C.

Agricultural

Determination of Selenium in Plant Material by the Codeine Test. J. Davidson. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 450–458.)—The plant material (10 g.) is digested in a large Kjeldahl flask with 75 ml. of conc. sulphuric acid (60 ml. for a 5 g. sample and 25 ml. for a 2 g. sample) and 0·7 g. of mercuric oxide. Frothing is avoided if the sample is in a coarse, unground condition and if the external source of heat is removed at intervals. Standard solutions containing 20 to 200γ of selenium are mixed with selenium-free material similar in kind and equal in weight to the sample and treated similarly. If such selenium-free material is not available, an equal weight of the sample is mixed with monopotassium phosphate and ignited at 700° C., and the resulting ash, which is now free from selenium, is put into the digestion flask (containing the standard solution) towards the end of the digestion process. If the sample contains but little iron, it is necessary to add 1 ml. of 0·5 per cent. ferrous sulphate solution to the sample and standard before digestion is completed. The residues in the Kjeldahl flasks are cooled, made up to the same volume, and allowed to stand overnight in order that as much mercury salt as possible may separate out. Aliquot portions, of about 20 ml., are removed without disturbing the precipitate (filtration by suction through asbestos may be necessary in some instances) and, after treatment with 5 or 6 drops of a 2 per cent. codeine sulphate solution, are allowed to stand in stoppered flasks for 2 hours. The amount of codeine added should not be less than 30 times the amount of selenium present in order to form the stable blue colour and not the less stable green colour. The sample solution is then compared in Nessler tubes, or preferably in a colorimeter, with the standard solutions. The amounts most conveniently determined in a colorimeter are from 2 to 8 parts of selenium per million of sulphuric acid. The standard solutions are made by dilution of a stock solution prepared by dissolving 1 g. of selenium in conc. nitric acid, evaporating nearly to dryness, and dissolving the residue in a litre of water. Vanadium, which gives a colour similar to that given by selenium, is seldom found in plant material. If, in exceptional instances, sufficient is present to interfere with the test, the difficulty may be overcome as follows:—A weighed quantity of the material is ignited with monopotassium phosphate at 700° C. to expel selenium. The vanadium in the residue is determined by the codeine test against selenium standard solutions, and the value found is deducted from the amount of selenium found in the sample. Alternatively, the ash, similarly prepared from a quantity of material equal to the amount taken for the determination of selenium, may be added to the standard solution before completion of the digestion with sulphuric acid. The accuracy of the method was established by determination of known amounts of selenium added to wheat. Various weights of a sample of flour containing selenium gave the following figures (parts per million):—19, 20·7, 18·8, 20. Four samples of wheat grown in seleniferous soil gave 25, 23, 13 and 22 parts of selenium per million respectively. Results obtained by this method agreed satisfactorily with those obtained by the method of Robinson, Dudley, Williams and Byers (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 274). A. O. J.

Organic

Use of Reinecke's Reagent for the Detection and Determination of Organic Nitrogen Bases. P. Duquenois and Mlle. Faller. (*Bull. Soc. Chim.*, 1939, **6**, 998–1008.)—Christensen's work on Reinecke's salt, $Cr(NH_3)_2$, $(SCN)_4NH_4$, H_2O (*J. prakt. Chem.*, 1892, **45**, 356), has been amplified and the conditions of precipitation examined. Amines and heterocyclic nitrogen bases as salts, such as pyridine, picoline, etc.; amino alcohols where the amine group is secondary or tertiary; alkaloids and proteins (ovalbumin, ovoglobulin, etc.) are precipitated. Peptone, guanidine, primary aliphatic amines are incompletely precipitated after some time (cadaverine is, however, completely precipitated after 24 hours). No insoluble reineckates are given by hydrocarbons, halogen derivatives, alcohols, aldehydes, ketones, acid esters, phenols or their immediate derivatives. Precipitation is usually carried out according to the directions of Kahane (*J. Pharm. Chim.*, 1935, 22, 254) whereby a cold saturated solution (about 40 per cent.) of the reagent is added in slight excess to a neutral or slightly acid solution of the base. The temperature of precipitation is that of ice-water; the precipitate is left a few hours, washed with ice-water, alcohol and ether, and dried at 65° C., or *in vacuo*, and weighed. In an investigation of these conditions it was found that to obtain a solution of Reinecke's reagent of about 40 per cent. strength it is necessary to heat, cool and filter. Precipitation was found to be more complete at 0° than at 15° C., and in the numerous instances in which a slightly acid medium is required, a drop of dilute hydrochloric acid causes immediate formation of the precipitate. Since most of the reineckates are soluble in varying degrees in 95 per cent. alcohol, washing of the precipitate by alcohol is not recommended, and a few reineckates are also slightly soluble in ether, *e.g.* histidine reineckate. Drying is best done in a desiccator for 6 to 8 hours, and then for 8 hours in an oven at 40° C. A porous glass plate is recommended for filtration. Thirty alkaloids and 20 amino bases have been determined by means of the Reinecke reagent and the results compared with those obtained by other methods, particularly the silicotungstic method. Bases precipitated quantitatively included hyoscyamine, homatropine, scopolamine, cocaine, emetine, quinine, quinidine, cinchonine, cinchonidine, morphine, papaverine, strychnine, brucine, pilocarpine, sparteine, stovain, nicotine, cicutine, pyridine, trigonelline, choline and cadaverine. Certain reineckates are too soluble in water to enable the precipitate to be used quantitatively, *e.g.* those of ethylamine, propylamine, allylamine, methylguanidine, methylecgonine, ecgonine and holocaine. Certain alkaloids with a lactone function, for which Bertrand's reagent is not suitable, may be readily and exactly determined with Reinecke's reagent. It is also very suitable for trigonelline and brucine, while creatine may be determined in presence of creatinine. Further, by making use of the pink colour of the Reinecke salt it is possible to determine an amine base or an alkaloid by colorimetric comparison with a standard. The grouping and form of the reineckate crystals allow of the detection of, for example, 1 part of brucine in 500 parts of strychnine; cocaine and its various derivatives give reineckates of very different micro-appearance, and morphine may thus be characterised in presence of other opium alkaloids.

D. G. H.

Eugenol in Essential Oil of Jasmine. S. Sabetay and L. Trabaud. (*Compt. rend.*, 1939, 208, 1242–1244.)—Essential oils prepared by different procedures by the firm of Bruno Court, Grasse, were found to contain 0·076 to 0·316 per cent. of eugenol.

S. G. C.

Po-Yoak Oil. A. Steger and J. van Loon. (*Rec. Trav. Chim. Pays-Bas*, 1938, 57, 620–628.)—The seed kernels of *Parinarium sherbroense*, a member of the *Rosaceae*, growing abundantly on Sherbro Island, Sierra Leone, yields an oil known locally as Po-yoak oil. A sample of the air-dried kernels yielded, on extraction with petroleum spirit, 40·6 per cent. of oil, and a further 3·6 per cent. on extraction with ether (corresponding with 26·4 per cent. on the whole nuts).

The oil was a pale yellow, viscous liquid which solidified to a buttery mass, even in the dark, when left in a tightly-closed flask. This semi-solid mass had to be heated for some time at 60°–70° C. before it became completely liquid again. The unpolymerised oil had the following characteristics:—Sp.gr. at 78°/4° C., 0·9250; acid value, 1·35; saponification value, 192·0; Reichert–Meissl value, 0·43; n_D^{18}, 1·5209; iodine value, Wijs (2 hours), 164; iodine value (120 hours), 250; thiocyanogen value, 76·1; diene value after 6 months, 60·0; after 3 years, 36·8. The fatty acids that had become polymerised into the form with higher m.p. were practically insoluble in petroleum spirit (unlike the acids of the original oil), but could be crystallised from carbon tetrachloride. The first main fraction had m.p. 102°–103° C., neutralisation value, 198, and molec. equiv. 292. Its composition corresponded with the formula $C_{18}H_{28}O_3$, and it was identified as the β-couepic acid occurring in oiticica oil. From the results of ozonisation it was concluded that it was a keto-elaeostearic acid with double bonds at the 9–10, 11–12, and 13–14 positions. The second main fraction crystallised from carbon tetrachloride had m.p. (not sharp) 72°–74° C. and n_D^{75}, 1·5011, and was found to be identical with β-elaeostearic acid from China wood (tung) oil. Po-yoak oil thus consists essentially of the glycerides of elaeostearic and couepic acids, and the differences between its sp.gr. and those of China wood oil and oiticica oil are to be attributed to the different proportions of elaeostearic acid in the three oils. Po-yoak oil dries rapidly in a thin film, and forms a good varnish when heated at 200°–300° C. On heating it gelatinises more rapidly than oiticica oil but less rapidly than tung oil.

Other *Parinarium* oils examined (*e.g.* néon oil) also contained elaeostearic and couepic acids in various proportions.

Inorganic

New Oxidation-reduction Indicators. G. Charlot. (*Bull. Soc. Chim.*, 1939, **6**, 970–977.)—The oxidation and reduction system taken for detailed study in connection with the indicators was $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$. In testing the suitability of new indicators, the oxidation-reduction potential must be determined in the neighbourhood of the colour-change, to ascertain the reactions for which the indicator can be used. Ferrous dimethylglyoxime is taken as an example, and details for the determination of this value and of the *p*H are given. It is shown to be a good reversible indicator and to be very sensitive, as 1 drop of $N/50$ solution is sufficient to give a perceptible tint, and it can be used for determinations in ammoniacal solution. The potential at the colour changes is +0·25 volt at *p*H 9·4. Indicators of oxidation and reduction reactions may be classified in three groups: (1) The functioning ions are inorganic, *e.g.* ferrous dimethylglyoxime, and sodium nitroprusside which, in alkaline solution, gives a very sensitive violet colour with sulphides, although the system is not reversible, and the potential at the colour change is 0·00 volt at *p*H 9·4. (2) Organic ions are involved, *e.g.* with diphenylcarbazide or diphenylcarbazone CrO_4'' ions give a violet colour in acid solution. Although not reversible, these indicators are useful in the determination of arsenic by means of bromine. Also, alizarine S gives with zirconium salts a red colour in acid solution. The system alizarine S—products of oxidation of alizarine S is irreversible, but the system alizarine S—products of reduction is partly reversible. These two systems may be used in acid solutions—the first at a potential of 0·95 volt, and the second at potentials of 0·25 and 0·35 volt. (3) Formation of a very stable complex, *e.g.* ferrous *o*-phenanthroline. A number of indicators used in connection with iron ions have been studied: Thioglycollic acid gives a violet colour with ferric ions at *p*H 7 to 10; the colour disappears by reduction at —0·20 volt, and at —0·25 volt there is reversible reduction of the thioglycollic acid; at +0·10 volt the colour is discharged by irreversible oxidation of the thioglycollic acid. Formaldoxime gives a violet colour in *N* sodium hydroxide solution with ferric ions; the colour is discharged by irreversible oxidation at +0·20 to +0·30 volt, and by partial reversible reduction of the indicator at +0·10 to +0·15 volt. Sulphosalicylic acid gives a violet red colour with ferric ions at *p*H3; colour change at +0·20 volt. Pyrocatechin gives a green colour at *p*H3; colour change at about 0·45 volt. 8-Hydroxyquinoline gives a green colour at *p*H 2 to 3; colour discharged by reduction of the ferric compound at about 0·60 to 0·70 volt. Pyramidone in *N*/2 hydrochloric acid gives a violet colour with ferric ions; colour discharged by reduction of the ferric compound at 0·60 to 0·70 volt. D. G. H.

Identification and Determination of Cerium in Small Quantities by means of Ferrous Ortho-phenanthroline. G. Charlot. (*Bull. Soc. Chim.*, 1939, **6**, 1126–1127.)—The determination depends on the strong oxidising properties of quadrivalent cerium in strong acid media. The indicator is prepared by dissolving 3 g. mols. of *o*-phenanthroline for every g. mol. of ferrous sulphate ($FeSO_4, 7H_2O$) the usual concentration being 0·025 g. $(C_{12}H_8N_2)_3Fe^{\cdot\cdot}$ per litre. The solid, or the solution, in *N* sulphuric acid is warmed with a little ammonium sulphate and sodium bismuthate (as oxidising agent) until a vigorous evolution of gas occurs; the mixture is then filtered and one drop of indicator solution is added. The solution becomes red in absence of cerium, and pale blue when it is present, and 2 to 3 mg. of cerium per litre may thus be detected. The only other common ions that would oxidise *o*-phenanthroline are MnO_4', Cr_2O_7'' and VO_3'. For a quantitative determination the cerium is oxidised as above to the quadrivalent condition in *N* sulphuric acid, and the solution of ferrous *o*-phenanthroline is added from a burette until a pink colour is formed. About 0·25 mg. of cerium may be determined thus in 100 ml. Manganese, chromium and vanadium interfere with the determination. D. G. H.

Determination of Aluminium in Ferrous Alloys. E. C. Pigott. (*J. Soc. Chem. Ind.*, 1939, **54**, 139–142.)—The method involves conversion of the iron into ferrocyanide and precipitation of aluminium by hydroxyquinoline, and is claimed to be applicable to iron and steel containing nickel, chromium, copper, cobalt, molybdenum, tungsten, vanadium, titanium, boron, beryllium, niobium, tantalum, selenium or tellurium. The time required is about 3 hours. For samples containing 1 to 12 per cent. of aluminium, a 0·5 to 1-g. sample is dissolved, as far as possible, in 20 to 30 ml. of *aqua regia*, and the liquid is evaporated to dryness. The residue is gently baked and dissolved in 20 ml. of hydrochloric acid, and the liquid is diluted to 80 ml., any precipitate being filtered off and discarded.

Chromium-rich samples are dissolved in dilute sulphuric acid; the solution is oxidised with nitric acid and evaporated to remove the excess of nitric acid; or the solution in dilute sulphuric acid is oxidised by boiling with addition of ammonium persulphate to convert chromium to chromate, and any precipitate of manganic hydroxide is dissolved by adding 1 ml. of hydrochloric acid. [Oxidation to chromate avoids the necessity for subsequently maintaining chromium salt in solution by a detrimentally large amount of tartrate.] The cooled solution, obtained by either method, is treated with 40 to 50 ml. of 20 per cent. tartaric acid solution, and then made slightly ammoniacal (1 ml. excess of ammonia); a solution of 20 g. of potassium cyanide for each 1 g. of sample is added, and the liquid is boiled for a few minutes. Any precipitate of manganese ferrocyanide formed at this stage is filtered off, after cooling to 40° C., and washed with tepid 10 per cent. ammonium chloride solution. The filtrate is heated to 60° C., and a moderate excess of hydroxyquinoline (10 per cent. in alcohol) is added. The precipitate of aluminium-hydroxyquinoline compound is filtered off and determined in the usual way. Titanium and uranium, if present, are precipitated with the aluminium, and the precipitate should then be dissolved from the filter in hot hydrochloric acid; 5 g. of tartaric are added followed by ammonia until the precipitate formed re-dissolves with difficulty. The temperature is adjusted to 60° C., and 50 ml. of 2 *N* ammonium acetate solution, together with about one-half the amount of hydroxyquinoline previously used (as 5 per cent. solution in 2 *N* acetic acid) are added; this precipitates the aluminium hydroxyquinoline compound. If zirconium or cerium are present in the sample, they should be separated before addition of tartrate-cyanide: zirconium, by precipitation with phosphate from the solution rendered 3 *N* in acid; cerium, by precipitation with oxalic acid in 0·5 *N* acid solution. S. G. C.

Specific Reagent for Ceric Salts. E. Montignie. (*Bull. Soc. Chim.*, 1939, **6**, 889.)—A reagent containing 0·5 g. of *p*-sulphanilic acid, 5 ml. of sulphuric acid and 100 g. of water gives a blood-red colour immediately and in the cold with concentrated solutions of ceric salts and with dilute solutions on warming. The coloured compound is stable and insoluble in ether and the colour is discharged by addition of sodium hydroxide. The limit of sensitivity is 20 mg. of cerium per litre. Persulphuric and periodic anions give a red colour with the reagent on heating, but this is always less intense than that given by cerium salts.

E. M. P.

Volatilisation of Metallic Compounds from Solutions in Perchloric or Sulphuric Acid. J. I. Hoffman and G. E. F. Lundell. (*Bureau of Stds. J. Research*, 1939, **22**, 465–470.)—The apparatus used was all glass and consisted of a distillation flask fitted with dropping funnel, leading-tube for entry of carbon dioxide, and exit tube connected with a water condenser, the outlet of which just dipped under water in a receiver. This apparatus is all sealed together. The chloride solution under test was introduced into the flask together with 15 ml. of perchloric (60 per cent.) or conc. sulphuric acid, or a mixture of 15 ml. of perchloric acid with 5 ml. of syrupy phosphoric acid. The liquid was distilled, and when the temperature of the contents of the flask reached 200° C. 15 ml. of conc. hydrochloric or conc. hydrobromic acid were added slowly during 20 to 30 minutes, a slow passage of carbon dioxide being maintained. The distillate and the residue in the flask were then examined to find how much of the element had distilled. The following results were obtained in distillations at 200° to 220° C.

Element	Approximate percentage volatilised from 20 to 100-mg. portions by distillation with—					
	HCl-$HClO_4$	HBr-$HClO_4$	HCl-H_3PO_4-$HClO_4$	HBr-H_3PO_4-$HClO_4$	HCl-H_2SO_4	HBr-H_2SO_4
Ag ..	0	0	0	0	0	0
Alkali metals	0	0	0	0	0	0
Al ..	0	0	0	0	0	0
As^{III} ..	30	100	30	100	100	100
As^{V} ..	5	100	5	100	5	100
Au ..	1	0·5	0·5	0·5	0·5	0·5
B ..	20	20	10	10	50	10
Ba ..	0	0	0	0	0	0
Be ..	0	0	0	0	0	0
Bi ..	0·1	1	0	1	0	1
Ca ..	0	0	0	0	0	0
Cb ..	0	0	0	0	0	0
Cd ..	0	0	0	0	0	0
Co ..	0	0	0	0	0	0
Cr^{III} ..	99·7	40	99·8	40	0	0
Cu ..	0	0	0	0	0	0
Fe ..	0	0	0	0	0	0
Ga ..	0	0	0	0	0	0
Ge ..	50	70	10	90	90	95
Hf ..	0	0	0	0	0	0
Hg^{I} ..	75	75	75	75	75	90
Hg^{II} ..	75	75	75	75	75	90
In ..	0	0	0	0	0	0
Ir ..	0	0	0	0	0	0
Mg ..	0	0	0	0	0	0
Mn ..	0·1	0·02	0·02	0·02	0·02	0·02
Mo ..	3	12	0	0	5	4
Ni ..	0	0	0	0	0	0

Element	Approximate percentage volatilised from 20 to 100-mg. portions by distillation with—					
	HCl-$HClO_4$	HBr-$HClO_4$	HCl-H_3PO_4-$HClO_4$	HBr-H_3PO_4-$HClO_4$	HCl-H_2SO_4	HBr-H_2SO_4
Os .	100	100	100	100	0	0
P .	1	1	1	1	1	1
Pb .	0	0	0	0	0	0
Pd .	0	0	0	0	0	0
Pt .	0	0	0	0	0	0
Re .	100	100	80	100	90	100
Rare earths	0	0	0	0	0	0
Rh .	0	0	0	0	0	0
Ru .	99·5	100	100	100	0	0
Sb^{III} .	2	99·8	2	99·8	33	99·8
Sb^{V} .	2	99·8	0	99·8	2	98
Se^{IV} .	4	2 to 5	2 to 5	2 to 5	30	100
Se^{VI} .	4	5	5	5	20	100
Si .	0	0	0	0	0	0
Sn^{II} .	99·8	100	0	99·8	1	100
Sn^{IV} .	100	100	0	100	30	100
Sr .	0	0	0	0	0	0
Ta .	0	0	0	0	0	0
Te^{IV} .	0·5	0·5	0·1	0·5	0·1	10
Te^{VI} .	0·1	0·5	0·1	1	0·1	10
Th .	0	0	0	0	0	0
Ti .	0	0	0	0	0	0
Tl .	1	1	1	1	0·1	1
U .	0	0	0	0	0	0
V .	0·5	2	0	0	0	0
W .	0	0	0	0	0	0
Zn .	0	0	0	0	0	0
Zr .	0	0	0	0	0	0

The work confirms that of Smith (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 360) that, by distilling with perchloric and hydrochloric acids, chromium can be separated from manganese in the analysis of steels containing high percentages of chromium. S. G. C.

Determination of Small Amounts of Iron in Tungstic Acid and Tungsten. M. L. Holt and D. Swalheim. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 254–256.)—The amount of iron considered was of the order of 0·001 to 0·007 per cent. Two methods are discussed: (*a*) precipitation of the iron as ferric hydroxide from a solution of tungstic oxide in sodium hydroxide solution; (*b*) an electrolytic method. The former having proved unsatisfactory, the following procedure has been worked out for the latter:—The tungstic oxide (8 g.) is dissolved in 75 ml. of 30 per cent. sodium carbonate solution; the iron remains dissolved as a complex salt. The solution is heated to 90° C., and electrolysed for 25 minutes with a platinum foil anode and copper foil cathode, both measuring 3 × 3 cm., at a current density of 10 to 20 amp. per sq.dm. The iron is deposited on the cathode as an iron-tungsten mixture containing 65 to 85 per cent. of tungsten. The copper cathode, with deposit, is then washed and dissolved in mixed nitric and hydrochloric acids, and the tungsten is separated as tungstic oxide by the usual method employed in steel analysis. The iron in the filtrate from the tungstic oxide is separated as ferric hydroxide by double precipitation with ammonia. In test experiments with methods (*a*) and (*b*) the ferric iron was finally determined iodimetrically. The results obtained on synthetic mixtures by method (*a*) were very slightly lower than by method (*b*); this was held to indicate that precipitation of traces of iron as ferric hydroxide by sodium hydroxide is not quite complete in presence of much sodium tungstate. For the analysis of tungsten powder the sample is first oxidised to tungstic oxide by heating in air. Tungsten in rod form was dissolved, as far as possible, by anodic solution in alkali. S. G. C.

Determination and Occurrence of Boron in Natural Phosphates and Superphosphates. L. F. Rader and W. L. Hill. (*J. Agric. Research*, 1938, **57**, 901–916.)—The Chapin methyl borate distillation method was employed in conjunction with the boric acid—mannitol titration. The results for acid-soluble boron (as B_2O_3) in natural phosphates ranged from under 10 to 144 p.p.m. (54 samples); in superphosphates, from under 10 to 158 p.p.m. (9 samples); in defluorinated phosphate rock from 20 to 30 p.p.m. (3 samples). S. G. C.

Physical Methods, Apparatus, etc.

Cobalt Compounds as Temperature-indicating Coatings. I.G. Farb. Akt.-Ges. (*Eng. Pat.*, 506,201, 1938; *Chem. Trade J.*, 1939, July 14, p. 31.)—This firm has already claimed as temperature-indicating coatings (*Eng. Pat.*, 478,140) substances containing metals which produce coloured oxides, and which when heated evolve at least one of the following compounds:—ammonia, ammonium derivatives, water or carbon dioxide. Compounds specifically mentioned are the simple and double ammonium salts or amines of elements which produce coloured ions; those compounds of metals having coloured oxides which contain water of crystallisation, or else water and/or carbon dioxide in a combined form, *e.g.* hydroxides, hydrated oxides, acid and basic salts, and normal, acid and basic carbonates; substances which belong to both of the above groups, *e.g.* amines containing water of crystallisation and double carbonates containing the ammonium radical. It is now found that certain of such substances (*e.g.* compounds of nickel or cobalt which contain water of crystallisation and also hexamethylene tetramine) evolve water of crystallisation at definite temperatures, and then show a sharp change in colour. In contrast, however, with most substances of this type, contact with moisture or with moist air gradually reverses the colour-change, although the change is irreversible in a dry atmosphere. In the following examples the formula of the compound, and the temperature and nature of the colour-change are given in order:—$CoCl_2,2C_6H_{12}N_4,10H_2O$, 35° C., rose to blue; $CoBr_2,2C_6H_{12}N_410H_2O$, 40° C., rose to blue; $CoI_2,2C_6H_{12}N_4,10H_2O$, 50°C., rose to green; $Co(CNS)_2,2C_6H_{12}N_4,10H_2O$, 60° C., rose to blue; $Co(NO_3)_2,2C_6H_{12}N_4,10H_2O$, 75° C., rose to purple; $CoSO_4,C_6H_{12}N_4,9H_2O$, 60° C., rose to violet; $NiCl_2,2C_6H_{12}N_4,10H_2O$, 60° C., pale green to yellow (100° C., yellow to violet); $NiBr_2,2C_6H_{12}N_4,10H_2O$, 60° C., pale green to blue. Although these compounds are soluble in water, they may be used in coatings with film-forming substances, particularly in the presence of inert pigments (*e.g.* titanium white). Their properties may also be modified by the formation of mixed crystals with other compounds given in the list, or with other isomorphous substances. Mixtures of such substances may be used for the purpose of indicating a number of temperatures by means of a single coating. J. G.

Reviews

SPECTROGRAPHIC ANALYSIS IN GREAT BRITAIN. Pp. 80. Royal 8vo. London: Adam Hilger, Ltd. 1939. Price 7s. 6d.

The enterprise of Messrs. Adam Hilger, and the editorship of Mr. G. C. Candler, have placed before us a survey of spectrographic analysis as applied by industrial firms, research organisations and laboratories throughout Great Britain. Those of us who have long advocated the use of spectrographic methods by chemists are entitled to some small measure of satisfaction in contemplating the widespread and increasing use of the method.

The monograph gives an account of the uses of spectrographic analysis by no less than 28 institutions, the subjects dealt with including metals of all kinds, minerals, sands, glasses, soils, plant extracts, paints and varnishes, archaeology and forensic investigations. This is an impressive record. It is but right that we should realise that this country was one of the earliest (I think, the first) to make spectrographs for industrial use. The record now given does tardy justice to British chemists for their foresight in adapting spectrographic methods to their problems. Little has been done by academic workers in this country to pursue this work, and in this respect we have fallen behind other countries.

It should by now be well appreciated that when repetition analysis of metals for control of their purity is required the spectrographic technique is indicated. Particularly is this so when high-purity metals or alloys are being produced. When the requisite sets of standards have been investigated and the conditions for the best method of application—arc or spark—have been worked out, there is available a rapid, accurate and inexpensive process for works control or research. The monograph before us points out the great variety of subjects to which these remarks may be applied fairly. Enterprising authorities who may read the accounts of uses collected by Mr. Candler will surely find themselves urged to take up spectrographic analysis at the earliest moment.

Messrs. Adam Hilger exhibit a modesty, unusual in manufacturing firms, in that they fail to point out that the possibility of applying spectrographic methods, to the extent now employed here, is in large measure due to their own activities in devising and making the necessary equipment, and also to their readiness to place their services at the disposal of chemists. J. J. Fox

LEHRBUCH DER ANORGANISCHEN CHEMIE. Prof. Dr. ERNST H. RIESENFELD. Second Revised Edition. Pp. xxvii + 706. Vienna: Franz Deuticke. 1939. Price M.14; bound M.16.

The ever-increasing pace of scientific discovery necessitates the issue, at intervals of only a few years, of text-books providing a reliable survey of most recent progress. In the domain of inorganic and general chemistry this task has been admirably fulfilled in the work under review. Although in its second edition, Professor Riesenfeld's book has not been previously reviewed in the pages of THE ANALYST. A brief reference to the plan of the work may therefore be welcome.

The author has set himself the task of presenting the subject on the basis of the new knowledge of atomic structure, the Periodic Classification being no longer regarded as the crowning achievement of inorganic chemistry, but merely as a foundation for further progress. Much importance is attached to general considerations on each group of elements, but the treatment of the more important compounds of the elements follows the conventional lines, the text being subdivided into short monographs.

The main subdivisions of the book are: Water and its Constituents; Non-Metals; Half-Metals; Metals; Noble Gases. The subdivision into non-metals, half-metals, and metals strikes one as rather arbitrary or artificial; the class of half-metals is limited to the five elements arsenic, antimony, silicon, germanium, and boron. Surely the more philosophical view is to regard the transition from non-metallic to metallic elements as gradual, without any demarcation justifying the above subdivision. Also it would be legitimate to include tellurium with the half-metals, while boron and silicon are usually regarded as definite non-metals.

However, the practical outcome of the adopted subdivision is mainly this—that it determines the sequence in which the author deals with the elements. It is the more minute details of which the text is made up that constitute the merits of this book, and among these the following:

The geochemistry of each element is adequately treated, it being impressed upon the student that the mineral kingdom is the ultimate source of the materials of inorganic chemistry. The lithophile, chalcophile, or siderophile character of the elements is brought out, based partly upon the results of the study of meteorites.

The text is interspersed with numerous and extensive passages in italics, expounding all the fundamental concepts of physical chemistry. The modern atomic theory, the electronic theory of valency, the various forms of space lattices, the constitution of double and complex salts, steric isomerism, radioactivity, isotopes and heavy water, biochemical data and the cycles of the important elements in the economy of Nature—all these and many other aspects of modern chemical knowledge are presented in most readable form.

As the author invites suggestions for improving the text, attention may be drawn to a few questionable or incorrect statements. Neodymium, which is about twice as plentiful as praseodymium, is represented as being much rarer than that element (p. 484); ruthenium is stated to be soluble in *aqua regia* (p. 599). The name columbium is alleged to be used exclusively in France (p. 501)—a statement betraying scant regard for Marignac's writings. Sodium carbonate solutions are said to deposit the "calcined" or anhydrous salt above 30° C. (p. 393). An etymological mistake occurs in p. 573, where the derivation of the term "prussiate" is given as *pruna*, a plum, instead of prussic acid, Prussian blue. The priority for the tannin separation of tantalum from niobium belongs to Powell and Schoeller (1925), but the text accords it to Viktor Schwartz, 1934 (p. 503). About half-a-dozen misprints and a few misspelt foreign names were noticed.

It is no exaggeration to say that the work under review, with its adequate subject index of 21 pages, is a portable encyclopaedia of general modern chemistry indispensable alike to the student and the more mature professional man. An English translation would be more than welcome. W. R. SCHOELLER

INORGANIC SYNTHESES. Vol. I. Editor-in-Chief: H. S. BOOTH. Pp. xiii + 197. London: McGraw-Hill Publishing Co., Ltd. 1939. Price 18s.

It is not quite clear to what type of chemist this book is addressed. The preface says that in 1933 "a group of inorganic chemists decided that there was a vital need for a series of volumes giving detailed and tested methods for the synthesis of inorganic compounds," and leaves it at that. This suggests something in the nature of an encyclopaedia of inorganic synthesis, but the book under review seems to make no claim to be any such thing; on the other hand, it does not appear to make any special appeal to the only chemist who synthesises simply for the sake of synthesis, namely, the student, and it is most catholic in outlook, passing from amalgams to bromopentammino cobaltibromide and taking fluorine, rhenium pentachloride and the extremely unstable azido dithiocarbonic acid in its stride. This having been said, however, one must hasten to add that the book is exceedingly good, and no better guide to a preparation could be desired, if one is lucky enough to find the substance one wishes to prepare among those given. As it is the first volume of an apparently protracted series, it seems likely that the grounds for criticism will be largely removed, but a general index to all the volumes will be a necessity.

Of the 67 syntheses described, a few are not syntheses in the ordinary sense of the word; for example, (1) purification of lithium carbonate, (2) purification of silver residues, and (67) a laboratory cement; the remainder, as has been mentioned, vary widely, with a slight, but perfectly natural, predilection for the unusual. One striking feature, which might with great advantage be widely copied, especially in books on analytical chemistry, is that, in the words of the preface, "each synthesis in this volume has been carefully checked in the laboratory and usually in a laboratory other than that in which the synthesis was initiated." In almost every instance the yield of the synthesised product is given, and in many the degree of purity to be expected, and the descriptions are so clear and concise that no difficulty should be experienced in following them. Apparently the last chapter in each volume in the series is to be devoted to the preparation of substances of technical use in the laboratory; in this instance a laboratory cement is the substance selected. The volume is well produced, printing, binding and proof reading being alike excellent, and there are two indexes—one of subjects, the other of contributors (*i.e.* those who have submitted or checked the processes).

There seems to be a real need of a book containing methods of preparation of representative compounds of all the elements in a state of such purity as to enable them to be used as standards; possibly the further volumes promised will make this book capable of fulfilling that very useful purpose. Meanwhile one may congratulate the editors on this excellent, if somewhat haphazard, start, and wish the series God-speed. B. S. EVANS

SYSTEMATIC QUALITATIVE ANALYSIS. By H. MIDDLETON, M.Sc., A.I.C. First Edition. Pp. viii + 279. London: Edward Arnold & Co. 1939. Price 8s. 6d.

Most chemists at some time or other have fallen under the spell of qualitative organic analysis. There is something about the subject that gives it a wider appeal than its more prosaic counterpart in the inorganic field. Perhaps it is that organic analysis has never been cribbed, cabined and confined, and still demands a facility for devising the right experiments and the ability to reason and draw deductions from the results so obtained. Yet it is clear that some sort of system is a great help and indeed essential. In his new book, Mr. Middleton outlines such a system, but fortunately it is neither rigid enough nor fool-proof enough to make the subject altogether devoid of adventure.

The first step in the scheme comprises the identification of the elements present in an unknown compound, the second the examination of its behaviour towards water, and the third the use of reactions to determine the chemical group to which it belongs. Once this is established, it is a comparatively simple matter to run through the lists of melting- or boiling-points that are given and confirm the identification of the substance by more specific reactions.

In the reviewer's opinion, the weakest part of Mr. Middleton's book is the important, indeed, the fundamental chapter, on "Class determination." The system of numbering and dividing into paragraphs is misleading and needs revision to make the scheme quite clear. The use of a "genealogical tree" would be of considerable help, as would the use of bolder type for the names of the groups into which substances are classified as a result of the reactions applied to them. Otherwise the book is to be commended for the comprehensive list of compounds that it deals with and for the completeness of its treatment.

There is a good index of substances that makes reference an easy matter, and in addition a most useful index of organic processes that facilitates reference to the reactions by which derivatives are prepared. The book can be recommended most warmly to students as a guide through the difficult labyrinth of qualitative organic analysis. The paper, printing and binding are of high quality.

F. A. ROBINSON

SCOTT'S STANDARD METHODS OF CHEMICAL ANALYSIS. Edited by N. HOWELL FURMAN, Ph.D. Two Volumes. Pp. xxxi + 1234 and xxi + 1317. London: The Technical Press, Ltd. 1939. Price £3 17s. 6d.

If it were possible to formulate a definition of a "standard method" that would satisfy all analytical chemists, it would greatly facilitate a description of the contents of this book and simplify the work of a reviewer. Thus a standard method might be one adopted by a society interested in a particular branch of analytical chemistry; one devised for internal use in an industrial firm; one arrived at by mutual agreement between buyers and sellers of some particular product or raw material; one that has been used by a recognised authority in some special branch of chemistry; or simply one that has become sanctioned by time and common usage. The present work contains examples of all these types, mostly from American sources. They share the common characteristic that they have all been selected as the best available for some particular purpose, but it is obvious that such methods are not of necessity the best for all purposes or fixed for all time, and the selection of a "works method" sometimes represents a compromise between accuracy, cost and speed.

When one considers the wide range covered by the two volumes of this work and the amount of new material and rewriting of old that distinguishes this, the fifth edition, from the fourth, the amount of discrimination that has been exercised in the selection of matter for inclusion is very striking; it would be safe to say that one could hardly take a problem in inorganic analytical chemistry to "Scott" without finding something very much to the point.

The value of the work to the general chemist lies in the prominence given to methods for the separation of the desired constituent from complex mixtures and interfering substances, especially in connection with commercial products. The determination of those elements sometimes described as "rare" has not been neglected, either when considered as main constituents, traces or interfering substances.

While retaining the old arrangement of subject matter instituted by Professor Scott, the work has been re-set on a slightly larger page. In the first volume the subject matter is arranged alphabetically under the names of the elements; each is treated separately in a monograph divided into sections dealing with general methods of detection, determination and separation, followed by gravimetric, volumetric and colorimetric methods, and determination in ores, alloys or industrial products. This simplicity of arrangement, combined with a complete author and subject index to the whole work in each volume, greatly facilitates its use as a work of reference. As compared with the fourth edition, the text has been increased by over sixty per cent., fairly equally divided between the two volumes.

The first volume treats of sixty-six elements, *i.e.* the international list minus the inert gases and parts of the rare earth and radioactive series. New monographs include niobium (columbium) and tantalum, by Dr. Schoeller—covering the complete work done by him and his numerous collaborators under the Analytical Investigation Scheme of this Society,—gallium, germanium, hydrogen, oxygen, rhenium and hafnium. The second volume, dealing with special subjects, is divided into two parts. The first includes methods of sampling; analysis of iron, steel and ferro-alloys, bitumen, cement, fuel, explosives, petroleum; oils, fats and waxes, paints, paper, poisons, rubber, soap and water: the second part deals with chemical procedures, and includes electrometric methods, gas analysis, chemical microscopy (by Chamot and Mason; with a reference to Wallis's *Analytical Microscopy*, now, alas, out of print), microchemical analysis, metallography and spectrographic analysis.

Of a work that includes so much, and in which the difficulty of selection is obviously so great, it is perhaps captious to complain of what is left out; but amongst such, one may perhaps be forgiven for mentioning S. G. Clarke's colorimetric method for determining small quantities of antimony (ANALYST, 1928, 53, 373) and R. E. D. Clark's colorimetric method for the detection of tin with 4-methyl-1:2-dimercaptobenzene (ANALYST, 1936, 61, 242), both of which have filled a real need. As an instance of a need having been filled in the reverse direction there is the reference to "Scott" (ANALYST, 1933, 68, 733) by Lampitt and Rooke, to a method for the determination of lead in connection with its occurrence in canned sardines, at a time when the literature on the determination of lead in traces was less voluminous than it is to-day.

In this edition the methods in Vol. I, Part I, are offered without qualification, whereas in the fourth edition they were described as "technical methods." As most of those in this section are used in industry, and the majority of the contributors are works chemists, they are properly so described, the adjective not implying deprecation; some works methods represent the highest degree of accuracy that it is possible to attain; the accuracy of almost all can, moreover, be determined to some limiting value; and to do so, whether he takes them from these pages or devises them for himself, rests with the user. For many purposes besides those of the works chemist the accuracy of a method is often of less importance than a knowledge of the extent and direction of its error. The description of many of these methods includes useful notes on the accuracy attainable; but exception may be taken to those in the section on non-ferrous alloys, where the criterion is concordance between duplicate determinations. Such concordance is a measure only of the precision of a method, and not of its accuracy, or the degree of concordance between the "result" and the true value. There is probably no branch of analytical chemistry in which the supposition that concordant duplicates imply accuracy is more likely to lead to error than the analysis of non-ferrous alloys.

Examples of loose writing occur in places, and there are some errors, such as that on page 480, where the lettered description of a burette for titanous chloride has no bearing upon the figure depicted. The methods described do not, in general, include those used in the examination of food; hence the inclusion of saponification by means of alcoholic potash in the determination of the Reichert-Meissl value, instead of the almost universally used solution of sodium hydroxide in glycerol, introduced by Leffmann and Beam more than thirty years ago, has probably been overlooked in the revision.

New editions of established works on analytical chemistry are of value mainly in that they present a survey of such methods of analysis as have received the sanction of usage, and thereby form a compendium of accepted data upon which further advances in technique may be based. In so far as they tend to become collections of time-honoured recipes to the exclusion of more recent improvements they outlive their usefulness.

Notwithstanding these few criticisms, the amount of new matter that has been introduced, and the thorough way in which the old has been revised, should ensure for "Scott" a continuance of the popularity that it has enjoyed for so long in its own special sphere as a text-book of general analytical chemistry.

F. L. OKELL

HANDBUCH DER LEBENSMITTEL-CHEMIE. Edited by A. JUCKENACK, E. BAMES, B. BLEYER, and J. GROSSFELD. Berlin: J. Springer.

Volume IV: FATS AND OILS. Pp. 966. 1939. Price: Stitched, RM.135; bound, RM.138.60.

Volume V: CEREALS, HONEY, SUGAR, FRUITS AND VEGETABLES. Pp. 1048. 1938. Price: Stitched, RM.135; bound, RM.138.60.

Volume VIII [i]: WATER AND AIR. Pp. 745. 1939. Price: Stitched, RM.108; bound, RM.111.60.

If a book is a really good one its value to the practical chemist increases as he becomes familiar with it. Repeated use leads to an appreciation of what it contains—and sometimes to realisation of its shortcomings. As the present series expands it becomes of greater value and, now that it is nearly complete, it is possible to refer from volume to volume and so to realise what great scope has been combined with attention to detail. The founders, Drs. Bömer, Juckenack and Tillmans, planned eight volumes; alas, two of the founders have died, but their successors, Drs. Bames, Bleyer and Grossfeld, have followed the same plan. It has, however, been found necessary to issue Volume VIII in two parts, one yet to come.

Volume IV treats of fat and oils, including therewith the lipins, waxes, resins and essential oils. It is one of the best volumes of the series. We observe that it adequately mentions both German and non-German work, and that it is quite up-to-date. Even Böseken and Cohen's (1938) work on sesamin, for example, is considered. The first section, by Bömer and Grossfeld, is of about 350 pages, mainly concerned with analytical methods. Almost every known process of any merit is included, and when one has a knotty problem in the examination of a fatty food help will almost certainly be obtainable here. We note in it, too, sections on semi-micro methods for the Reichert value and a micro-technique for determining the melting-point of the sterol acetates, which requires less than a gram of fat. Methods for the determination of individual fatty acids are given in many instances, and such matters as differential halogen absorption are clearly set out. Hilditch's now world-famous methods and results are summarised.

The same authors provide detailed descriptions of individual oils and of special analytical methods appropriate to them. There is also interesting information on the constituents and food values of different margarines and of hardened oils. Help is also available on the, sometimes difficult, examination of lard.

Dr. Griebel supplies details of the macro and micro structure of oil seeds and edible nuts. Dr. Halden follows with chapters on sterols, and Dr. Grau on the waxes and essential oils. Then there are, as in other volumes, summaries of German and foreign law relating to the subject. The whole volume is very well done; no important matters seem to have been omitted.

Volume V. This volume is the work of nine authors; it deals with cereals, bread, honey, sugar, jam, fruit, confectionery, and vegetables. Under such conditions it is, perhaps, unavoidable that there is some overlapping and a few omissions. It is necessary sometimes to make cross references to find all one wants to know about a particular topic, but when this is done the work proves to be quite a mine of information. We note with interest that "Mehlverbesserung" with chemicals is not favoured in Germany, and that it is intended ultimately to forbid it; how desirable this is becomes obvious when one reads of the use even of vanadium salts for this purpose. The volume includes detailed descriptions of all products comprised under the main headings given, and the illustrations are good. Under honey there are drawings of 64 kinds of pollen grains which may be identified. There are references to all the enzymes and to unusual or poisonous types, such as Noors honey. Sugar and the manufacture of its various kinds are considered in some detail, and there are also special methods of analysis applicable to these products; general sugar methods have been dealt with in Volume II.

Berries, fruits, nuts and their products are illustrated in detail, though no reference to barium in Brazil nuts, or to the de-bittering of almonds, was found. The section on jams is valuable, but must be used with caution, because jam on the Continent is not always the same as it is to us. The best Konfiture may contain two parts of fruit to one of sugar, whereas most of the ordinary marmalade has equal parts of fruit and sugar. Our full-fruit standards are not quoted, and there is but little direct instruction on the determination of the fruit-content. On fruit juices there is much that is helpful—the commercial development of these is well advanced in Germany. The sections on the chemistry and microscopy of the vegetables, including truffles, mushrooms and fungi, is thorough and well illustrated. As a whole, there is more descriptive matter and less chemical theory in this volume than in Volume IV.

Volume VIII [i]. This volume, on the technology of water, is by Drs. Sierp and Splittberger, the law being dealt with by Dr. Holthofer. The subject matter is concerned with the collection, purification and treatment of drinking water with industrial water supplies, and with effluents and trade wastes. Methods for the examination of waters, analysis, and the technology of mineral waters i reserved for Part [ii]. The reviewer knows of no other single volume which deal with this subject so exhaustively and discusses so many methods of treatment Storage, filtration, chlorination, ozone, katadyne, electrical processes, U.-V.-light treatment, and other less-known methods are discussed in considerable detail. The authors have perhaps an advantage in that on the Continent there is so great a variety of processes in actual large-scale use. The special treatment of water for particular industries is considered, and there is useful information on th removal of various minerals, correction of acidity, de-gassing, softening, base exchange, and treatment with synthetic resins. The work is thoroughly up-to-date.

The section on the purification of sewage effluents and of industrial waste liquors is very well done, and there is a wealth of illustrations of plant operating in particular works. The volume as a whole is good and can be commended to all who are concerned to know what methods are available and are used abroad, as well as to have a critical survey of methods familiar at home. H. E. Cox

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THE ANALYST

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Food Inspection and Analysis in Holland

By J. STRAUB, Chem.Ing.

(*Director of the Food Inspection Laboratory, Amsterdam*)

(*Read at the Meeting, April* 5, 1939)

As a member of your Society, it affords me great pleasure to give some account of my daily work in connection with food inspection and analysis. Some of you may have been present when a party of English food chemists paid a visit to my laboratory in 1936.

Food chemistry is a branch of applied science. That is to say, it is studied not for its own sake—simply for the pleasure of knowing so much more of Nature's secrets—but for the material benefit to mankind that is to arise from it. Scientific methods are used to solve chemical problems that have social results as an ultimate aim.

Research work in Holland offers several good examples of the fundamental rôle that analytical chemistry has played in advancing our knowledge of all branches of food chemistry. Thus, in the first place, I may mention the recent work of Jansen,[1] Professor of Physiological Chemistry in Amsterdam, who (with his pupils, Cohen, Wiegand and others) worked out a simple chemical method for the quantitative estimation of vitamin B_1 in food and in urine. This opened the way to the exact study of vitamin B_1 metabolism, and for work on the diagnosis, cure and prevention of B_1-avitaminosis. The vitamin is adsorbed on acid clay (frankonite) and oxidised to thiochrome, and the fluorescence of this substance in ultra-violet light is measured with the fluorometer of F. H. Cohen.*

At Utrecht University, Prof. Wolff and pupils have done much work on vitamins A and C. Existing methods of estimating these substances have been studied, simple chemical and micro-chemical methods for routine work have been worked out for vitamin A, for carotene and for vitamin C, and these methods have been applied to fruits and vegetables, milk and animal products, so that complete lists of the vitamin-contents of various foods could be compiled. This list proved to be of great value as a basis for a critical survey of the diet of certain groups of the population, especially the poorer classes and the unemployed, in Holland. The application of the methods to urine and blood affords the possibility of recognising malnutrition or incipient vitamin deficiency. A complete set of papers on the chemical estimation of vitamins has been published in the report of a meeting, held in 1938, of all Dutch workers in this field.[2]

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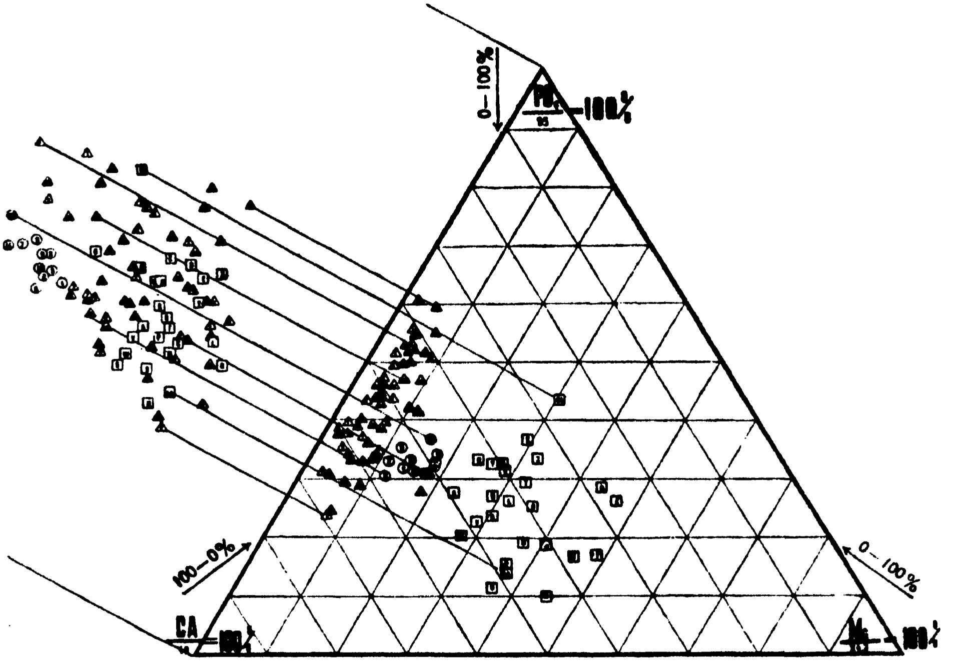
* Obtainable from Adam Hilger, Ltd.



O = healthy; normal.
□ = milk fever.
△ = grass staggers.

FIG. 1

Relative concentrations of Mg, Ca and PO_4 ions in blood serum of normal and diseased cows. The spots outside the triangle give the absolute values for Mg + Ca + PO_4 (B. Sjollema, 1929. Ref. 5).

Reference may be made also to the work of the Department of Veterinary Chemistry of Utrecht University, where the analysis of food, especially of cattle-food, has led to far-reaching results. Here Prof. Dr. B. Sjollema, Dr. L. Seekles and their co-workers found that various diseases of cows were specifically caused by deficiency of certain metals in the diet. Cows are particularly sensitive to small deviations in the mineral-content of the feed, because every day they excrete in their milk much mineral matter and many different elements, and so run the risk that their bodies may be entirely deprived of some indispensable constituent.

Various published methods for estimating traces of copper in grass and in the soil of meadows, in cattle-food, in milk and in blood were tested[3] and adapted to the material in hand (carbamate method, thiocyanate method). The copper-content of different samples showed wide variations. The endemic cow disease "pine" and also a newly observed disease with other symptoms were proved to result from copper deficiency. Sjollema[4] cured them by spraying a small quantity of copper sulphate on the meadow or by giving it to the cows.

Much work has also been done on the calcium, magnesium and phosphate contents of feeding stuffs and blood. Here, again, Sjollema[5] and Seekles discovered the cause and the remedy for two diseases. "Grass staggers" proved to be associated with magnesium deficiency, and milk-fever with relative magnesium excess. The results for the three constituents were plotted in triangular graphs, so that differences in the relation of the different ions could be easily seen (Fig. 1).

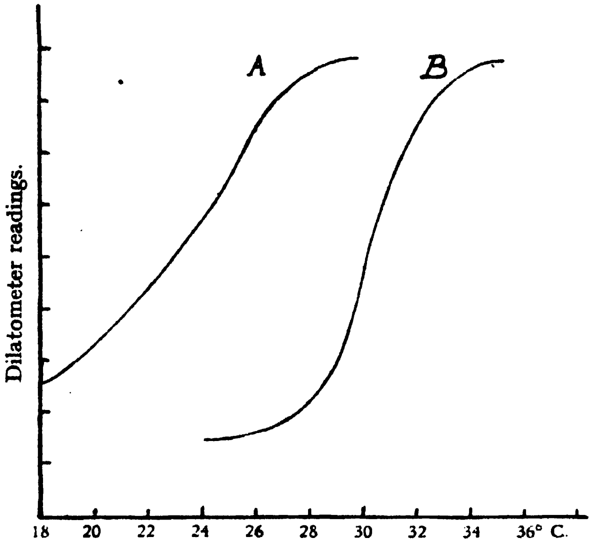


FIG. 2

Dilatation of cocoa butter with rising temperature, showing the effect of gradual melting. B is a curve for cocoa butter, recrystallised by keeping it in the dilatometer for 15 hours at 24° C. (J. D. van Roon, 1930. Ref. 14).

Apart from this University work, food research is carried out under the Department of Agriculture. I might remind you of the latest achievement of my friend Kruisheer,[6] who with his staff worked out a mechanical device for measuring the consistence of butter. The hardness or softness of butter is a somewhat important property in trade, although it has nothing to do with the taste and the nutrient value. Housewives are particular about it, as they have to spread the butter, and so the consistence has become one of the elements in grading butter for the grocery trade. Hence it is useful to have available an objective measuring instrument, which can also be of great service in investigations to improve the consistence of butter. Kruisheer's ingenious instrument gives an exact reading of the force used in pushing with a constant velocity a metal cylinder into the butter.

Kruisheer's former work on food analysis was done at the time he was a Public Analyst. His method[7] for estimating honey in honey-cake is generally accepted and gives accurate results. It is based on the fructose method first described by Kolthoff[8] (oxidation of aldose with excess of iodine and caustic soda, followed by quantitative copper reduction, preferably by Schoorl's method)[9]. His method for estimating hydroxymethylfurfural in wines, which has also met with general acceptance, has proved of great help in distinguishing genuine wines from products that have been sweetened with invert sugar or concentrated grape-juice. From this work he went on to devise methods for the estimation of laevulosin and inulin, which are useful in the analysis of coffee extract for chicory and caramel.[11]

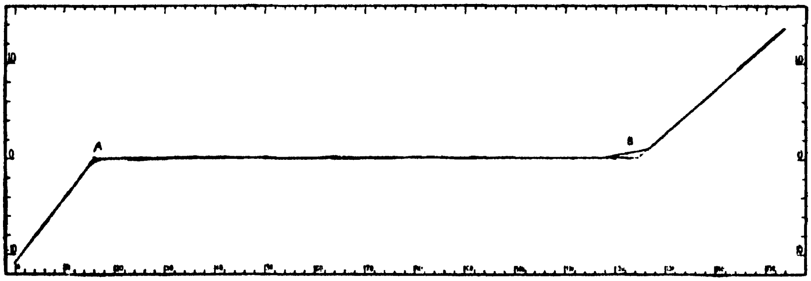


FIG. 3

Fusion line for 2·9 g. of ice, as used to check the calorimeter constants (Straub and Malotaux, 1933. Ref. 17).

Of late years food industry in Holland has occupied the attention of many chemists. Very little of their work, however, is published, although some good analytical studies have been made.

Ch. Doppler,[12] of the well-known Droste cacao mills, published analytical studies on cell-wall substances of the cacao bean.

Bertram,[13] formerly of van den Berghs, Ltd., published his now well-known permanganate method for estimating saturated and unsaturated fatty acids in fats, and the A and B number method for estimating butter-fat and coconut oil in margarine. He is also reputed to be the first inventor of a method of determining the solid-liquid partition in fats at different temperatures by means of the dilatometer. The method was devised independently and published by van Roon,[14] at that time chemist to van Houten's cocoa works (Fig. 2).

Other analytical work of importance to the fat industry has been done in the laboratories of Delft Technical High School and Rotterdam Trade University. Steger and van Loon[15] (Delft) published detailed modern analyses of various vegetable oils, including the determination of the content of oleic acid isomers, elaeo-stearic acids and couepic acid (= licanic acid). In Verkade and Coops's work[16] (Rotterdam) a method for analysing the very complex mixture of fatty acids of natural fats by fractional distillation of methyl esters and by physical analysis (melting-curve) of the binary mixtures that distil has been devised.

In this connection something may be said about the work of Malotaux[17] and myself on fats. We recognised long ago that the change of consistence with temperature was an important factor in the palatability of edible fats. Whilst van Roon used a dilatometric method to obtain numbers and graphs for this property in different fats, we made use of a calorimetric method. Both depend on the idea that one of the major elements in consistence is the proportion of solid to liquid glycerides in the fat. With rising temperature solid parts gradually melt, that is to say, they are dissolved in the liquid part. This change is accompanied by a change in volume and so can be followed by means of the dilatometer.

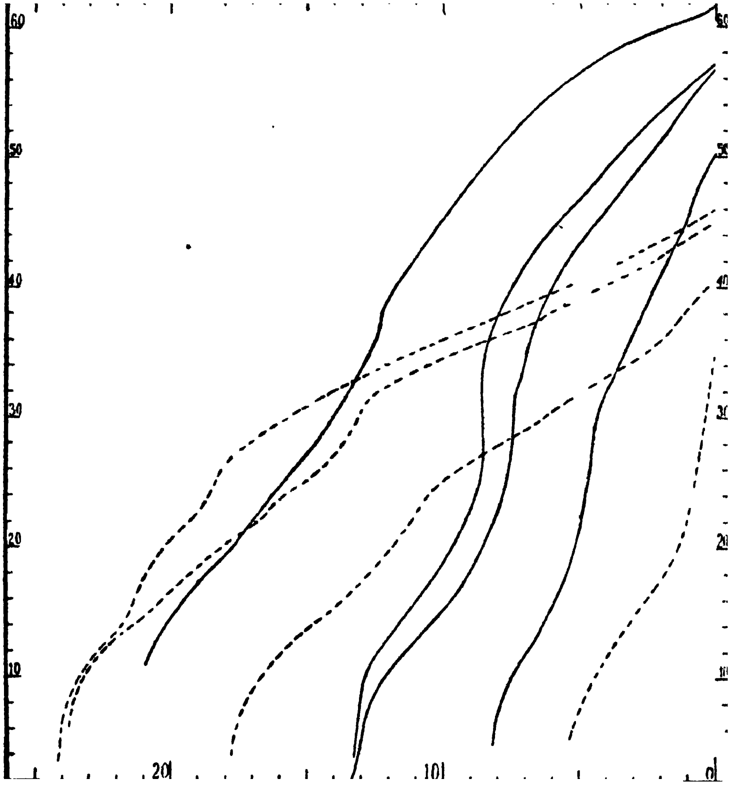


Fig. 4

Gradual change of consistence curve for sesame oil during hardening with nickel and hydrogen. The dotted lines and continuous lines represent two different hardening processes (Straub and Malotaux, 1933. Ref. 17).

It is also accompanied by an absorption of the heat of fusion and so can be followed calorimetrically. Although the apparatus is simple in principle, it must be very carefully made. The fat to be melted is put into a silver crucible; for better transmission of heat this cylindrical thimble contains a fine network of metal gauze. A thermometer is placed in the centre and the whole is fixed in a glass bulb; this is put in a water-bath together with a thermometer, and the test is started. The bath is heated in such a way that there is continually a difference of 10° C. between the two thermometers, and exact readings are taken every minute, a stop-watch being used.

After an hour the fat is fully melted and the readings are plotted as a graph. There is a horizontal time-axis and a vertical temperature-axis. Fig. 3 illustrates an experiment in which there is pure water in the thimble. Starting from −10° C., we have first the warming of the ice from −10° to 0° C., then at 0° C. complete melting, and lastly the warming of the water.

With the constant difference of temperature there is a constant transmission of calories, so that 1 minute means exactly 2 calories, 40 minutes indicate 80 calories, and 80 calories correspond with one gram of water melted. Thus the calorie scale is used as a quantitative scale for the solid-liquid transition. When the method is applied to fat it is advantageous to correct the curve, by subtracting from readings the known amount of heat necessary for warming the sample, and so to take into consideration only the unknown amount of heat used for melting.

An example will give some idea of the very specific results that the method gives. In the process of hardening fats, solid material is gradually formed. Samples of soya-bean oil, taken from the hardening drum every 15 minutes, were examined calorimetrically and showed lines grouped like the spokes of a fan (Fig. 4). Then a second method of hardening (at a different temperature and pressure) was followed, and quite another set of curves was obtained; this demonstrated that in the second method more solid (and with a lower melting-point) was formed, so that a much better product for edible purposes was obtained (see Fig. 4, dotted lines).

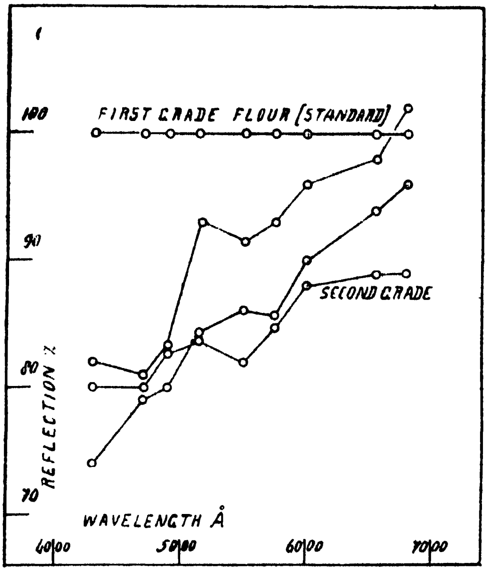


FIG. 5

Percentage reflection of light of nine different wave-lengths by first grade and second grade bakers' wheat flour (bleached) and by two intermediate samples. Differences amplified by the method of Straub and Simons. Filters and comparator of A. Hilger, Ltd.

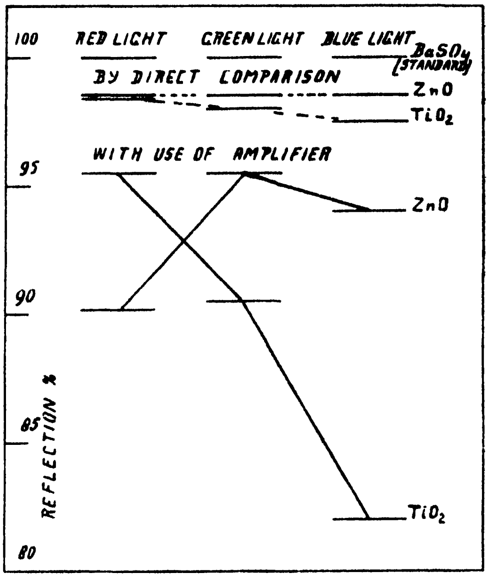


FIG. 6

Percentage reflection of red, green and blue light by ZnO and TiO_2 powders, measured by comparison with standard $BaSO_4$ powder (*a*) by direct comparison of flat surfaces, (*b*) with the use of Straub and Simons' amplifier.

There is yet another method used in my laboratory about which I should like to say a few words, the more so as I have found English instrument makers, Messrs. Adam Hilger, Ltd., willing to make the instrument required. This is a method for measuring the whiteness of such substances as wheat flour, paints or paper. I will begin by giving some experimental results in the form of graphs (Figs. 5 and 6). Good wheat flours of low, but somewhat varied, milling grade, and with ash-contents ranging from 0·3 to 0·6 per cent., show slight differences in whiteness, which can be seen by experts, but can hardly be measured colorimetrically except by very sensitive photo-electric cell methods. In simple subjective colorimetry the difference amounts to only about 2 per cent. with light of any colour. There is about the same degree of difference between white paints. With the simple instrument devised in collaboration with my friend, Mr. Simons, we amplify colour differences about tenfold, so that subjective colorimetry ten times as sensitive as the discerning power of the eye becomes possible. Readings are made from blue to red in the spectrum with a number of different light-filters. A heavily bleached flour of the very first grade and with low ash-content is used as a standard. The principle of the amplification is to bore a hole of well-defined dimensions in the flour samples and to measure the light reflected from the bottom of this hole.

The instrument, for which a patent application has been made, consists of two tubes for the flour samples, fixed in the bottom of a metal bulb painted white inside. A powerful electric lamp in the bulb supplies good indirect illumination. The whole is just an accessory to a colour comparator and may be called a colour "amplifier," as suggested by Messrs. Hilger (the instrument as made by them will have two lamps in the bulb). It is obvious that here, again, an analytical method gives a basis for research. In the quest for whiter material an exact means of measuring whiteness must first be found.

So much about methods of general interest used in my laboratory. Of course many special methods must of necessity be devised in the laboratories of Public Analysts. I might mention here some work of my predecessor, van Raalte, the simple xylol number method[18] for estimating the butter-content of margarine and the method of recognising refined lard by its fluorescence.[19] Regulations on the composition of foods are of no use if they cannot be maintained or enforced, and this cannot be done if there is no satisfactory method of analysis available to ensure that commercial products are up to standard. For example, a regulation to the effect that milk bread must be made with milk was issued, when Public Analysts had worked out an exact method for determining butter-fat in presence of other fats and milk sugar in presence of other carbohydrates.

Official methods are exactly described in the regulations and must be followed in so far as they are sufficient. Should they fail to disclose some new form of adulteration the analyst is at liberty to make use of his personal experience and resources. Many special methods have thus been devised or adapted to circumstances by our Public Analysts and have subsequently been included in the regulations for different foods; many, of course, have also been taken from the literature without any change and are the same as those used all over the world, such as, for example, the Feder number for added water in sausage, and the freezing-point for added water in milk.

There are now food regulations for every group of foods, all formulated on the same plan. First, they give the definitions of the various foodstuffs with which they deal, and prescribe the names under which these foods must be sold and labelled. Then they give the minimum analytical values permissible for each foodstuff, and lastly a precise description of the analytical methods to be used. Some of them also contain detailed requirements as to the dimensions and hygienic condition of shops and factories. As quite a new feature in this legislation I should mention that for some groups of packed foods the net contents must be stated on the package. The regulations promote general hygiene and protect the public from fraud and the trade from unfair competition. The intricate task of drawing them up is carried out by joint committees of government officials and leading manufacturers and tradesmen. Most of the regulations have now been in force for about ten years, and have become so accepted by the trade that only slight infringements occur, and these are mostly stopped by simple warnings. If necessary, legal action can be taken, jurisdiction being based upon the Food Act of 1919,[20] in which are laid down the principles on which the regulations are based. Other details and a summary of the chemical requirements for various foods have already been published in THE ANALYST by van Raalte and myself.[21] The Act also prescribes the organisation of control. The country is divided into 15 districts with a laboratory in each of them. From these centres inspectors pay systematic visits to control the hygienic condition of shops and factories in towns and villages, to inspect the soundness of foods in shops and markets, and to take samples of articles that cannot be judged on the spot. These inspectors must be keen and expert in their work. Especially difficult and responsible is the work of those who inspect game, poultry and fish, because their judgment cannot be supported by chemical evidence. This legal scheme of control seems to me to be analogous to what is aimed at under your new Food and Drugs Act. Therefore you may be interested to know how many officials have appeared to be necessary for food control in Holland. The Amsterdam district consists of the town itself and all neighbouring communities to a distance of 15 or 20 miles. The total number of inhabitants is one million. I have fifteen full-time inspectors for outdoor work, and of these, five are experts in milk, six in groceries and allied products, two in fish, one in bread, and one in game and poultry. The number of shops that one man can inspect thoroughly in a day is about 25; a market, of course, takes more time, whilst the stall of a street vendor takes less. The total number of visits in 1938 amounted to 64,000. The number of samples analysed in 1938 was 30,595, of which 24,387 were samples of milk and milk products. The numbers for 1937 are published in the February issue of THE ANALYST.[22] In addition to this staff of inspectors and analysts, there is a small clerical and general staff, including an instrument maker.

However, it is not easy to compute from the conditions in circumstances so different in Holland the number that would be required in England. Much depends on what articles are submitted to the control; thus, for example, drugs are not under our control in Holland, whilst, on the other hand, the Laboratory has recently been charged with the supervision of traders in gas masks, and the control of shops selling mattresses, bedding and bed covers, the filling material of which must now be declared on a label. As regards the number of laboratory workers much depends on the requirements for various foods laid down in the regulations and on the methods of analysis involved. In general, a new regulation demands more work both from the inspectors and from the analytical staff than one that has been in force for some years. Most important is the distinction between articles that have a long period of life such as groceries, canned foods and jams, and articles of which new lots are distributed or manufactured every day or week, such as milk, bread, ice-cream, sausages, fruit and vegetables, fish, game and poultry. This distinction must always be borne in mind, and by far the most attention must be given to the ever-changing stocks of perishable commodities.

I have learned much from English analytical work and I should be glad if, in my account of food inspection and control in Holland, I may have been of some service to English analysts in return.

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Manganese and Caffeine Contents of some Teas and Coffees

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(Work done under the Society's Analytical Investigation Scheme)

It is well known that tea contains an unusually high proportion of manganese as compared with other plant products; this manganese depends upon a relatively high proportion in the soil suitable for tea planting. Coffee and maté also contain manganese, though in smaller proportions. Hence it seemed possible and worth investigating if the manganese might be a factor affecting the synthesis of caffeine by the plant. It could hardly influence the formation of tannin, since other tannin-yielding plants do not show much manganese. The fact that tea and, to a less extent, maté and coffee, have in common relatively high proportions of caffeine and manganese suggested the possibility of a connection between the two; this survey was carried out with a view to ascertaining if any relation existed between the two constituents. The determinations were made on 15 samples of black teas and 6 samples of raw coffee beans.

Tea.—*Manganese.*—For the determination of manganese in tea, the method was based on that used by Broek and Wolff[1] for milk. It consisted in the destruction of the organic matter by nitric and sulphuric acids and subsequent oxidation of the manganese to MnO_4' by means of potassium periodate, the resulting colour being measured in a Lovibond tintometer.

To approximately 1 g. of the finely-powdered sample, weighed into a 500-ml. Pyrex Kjeldahl flask and moistened with a little nitric acid (reagent quality), was added 20 ml. of sulphuric acid (reagent quality), the mixture was heated to boiling, and more nitric acid was added dropwise in the usual manner. The addition of the nitric acid was continued until all organic matter had been oxidised and a colourless solution obtained on evaporating the liquid until white fumes appeared. One g. of potassium persulphate was added, and the solution was diluted and then evaporated to fuming. The cold solution was diluted and transferred to a 250-ml. conical flask, the Kjeldahl flask being rinsed with successive portions of water, until the volume of the mixture was about 100 ml. The solution was boiled to expel sulphur dioxide and cooled somewhat, 0·1 g. of potassium periodate was added, and the mixture boiled for a few minutes and then kept hot for half-an-hour to develop fully the pink colour. The resulting solution was diluted to a known volume (usually 200 ml.), and the colour was measured, in a Lovibond tintometer, in 50 ml. (or, if necessary, in a smaller volume diluted to 50 ml.). It was found advisable to re-develop the colour in the diluted solution, by heating with a small quantity of potassium periodate before taking the reading in the tintometer.

A calibration curve was obtained by treating 5 ml. of a manganous sulphate solution (0·1 mg. of manganese per ml.), prepared from standard potassium permanganate solution by reduction with sulphur dioxide, with 20 ml. of conc.

sulphuric acid and 50 ml. of conc. nitric acid (the amount usually employed in a destruction) and then proceeding as described above. The solution, after oxidation with potassium periodate, was diluted to 250 ml., thereby giving a solution containing 0·002 mg. of manganese per ml. Ten to 30 ml. of this solution were diluted to 50 ml., the colour was re-developed, and thus tintometer readings were obtained for concentrations of manganese from 0·02 to 0·06 mg. in the 50 ml.

A confirmatory series of determinations was carried out by the ashing process. One-gram samples of the teas, weighed into small silica basins and moistened with 1 to 2 ml. of conc. sulphuric acid were ashed at dull red heat in a muffle furnace. The residual white ash was dissolved in dilute sulphuric acid (15 ml. of conc. acid per 100 ml. of water), and filtered, the filter-paper was ignited, and the residue, if any, was dissolved in about 10 ml. of the diluted sulphuric acid; the solution was filtered into the main filtrate, which was then oxidised with potassium periodate. Tintometer readings were taken after suitable dilution and re-development as before.

Table I

Teas

Description.. ..	Ceylon O.P.	Ceylon B.O.P.	Assam B.O.P.	Dooars B.O.P.	Malaya B.O.P.	Travancore B.O.P.*	Japan Black	Keemun China
Moisture, per cent. ..	6·1	6·6	5·4	5·5	6·1	5·3	6·0	6·5
Caffeine, per cent. (on dried tea)	3·35	3·54	4·23	4·79	4·30	3·13	2·45	3·18
	3·27	3·47	4·18	4·80	4·43	3·21	2·43	3·27
	3·25	3·55	4·26	4·83	—	3·21	—	—
	—	—	—	4·80	—	—	—	—
Manganese, per cent. (on dried tea)								
Wet oxidation	0·0292	0·0271	0·090	0·0145	0·0184	0·0174	0·085	0·047
	0·0292	0·0269	0·089	0·0145	0·0182	0·0173	0·084	0·047
	—	—	0·090	—	0·0182	0·0175	—	—
Low temp. ashing ..	0·0291	0·0272	0·090	0·0147	0·0180	0·0172	0·083	0·048
High-temp. ashing	—	—	—	—	—	—	—	—

Teas—*continued*

Description	Sylhet B.O.P.	Java B.O.P.	Sumatra B.O.P.	Nyasaland B.O.P.	Nyasaland Fannings	Kenya B.O.P.	Assam B.P.
Moisture, per cent.	5·2	6·0	5·7	5·8	5·5	5·8	5·3
Caffeine, per cent. (on dried tea)	3·64	3·47	3·70	2·71	2·85	2·84	4·68
	3·66	3·42	3·72	2·74	2·90	2·91	4·74
Manganese, per cent. (on dried tea)							
Wet oxidation	0·053	0·0080	0·0145	0·089	0·057	0·138	0·031
	0·054	0·0079	0·0146	0·087	0·056	0·137	0·032
Low temp. ashing ..	0·052	0·0082	0·0148	0·089	0·057	0·135	0·032
High temp. ashing ..	—	—	—	—	—	—	0·031

* O.P. = Orange Pekoe; B.O.P. = Broken Orange Pekoe; B.P. = Broken Pekoe.

A calibration curve for this procedure was obtained by evaporating 5 ml. of the manganous sulphate solution (0·1 mg. of manganese per ml.) to dryness, adding 1 to 2 ml. of conc. sulphuric acid, and heating in the muffle-furnace at dull red heat for 3 to 4 hours. The residue was dissolved in the dilute sulphuric acid, the manganese was oxidised with potassium periodate, and the tintometer readings were taken as before.

It was found that heating in the muffle at bright red heat or treatment of the manganous sulphate directly with potassium periodate gave readings which agreed exactly with those obtained by the procedures previously described. Hence no loss in manganese occurs during either the wet oxidation or the ashing treatment.

In one experiment a sample of tea was ashed at the full muffle temperature, and the result agreed, within the limits of experimental error, with those obtained by the ordinary low-temperature ashing.

Caffeine.—The caffeine-content of the tea was determined by the Bailey and Andrew method.[2] The nitrogen-content of the impure residue of caffeine was determined by the usual Kjeldahl procedure, and the amount of caffeine was calculated from N × 3·464.

The results (Table I) are expressed as percentages on the dried tea, the moisture-content being determined by drying 1 to 2 g. at 100° C. Preliminary experiments showed that two hours' drying was sufficient to expel all the moisture.

COFFEE.—*Manganese.*—The manganese-content of coffee was determined by the ashing procedure, using 5 g. quantities of the coffee beans, broken in a porcelain mortar and mixed as thoroughly as possible. It was found that determinations on the powder obtained by grinding the beans in an ordinary coffee-mill usually gave higher results. This was found to be due to minute particles from the blades of the mill (filings of which were found to contain manganese). It was noticeable that with coffee beans which were brittle, and hence easily powdered, the results on the powdered samples agreed with those on the broken beans.

Some manganese determinations were carried out on the de-caffeinated residue obtained after chloroform extraction of the finely-ground coffee. These were found to agree, within the limits of experimental error, with those obtained on the original powder. Hence practically no manganese was extracted with the caffeine.

Caffeine.—The caffeine-content of coffee was determined on the finely-ground samples by the Gorter method. It was found that the original procedure[3] gave low and widely discordant results, and hence the caffeine was extracted from the fatty residue by boiling with water instead of treatment with hot water. This modification has also been described by Fox and Sageman.[4]

In the two determinations the nitrogen figure obtained from a Kjeldahl determination on the aqueous extract of the fatty residue was found to give a caffeine-content higher than that obtained from a Kjeldahl determination on the impure caffeine obtained by chloroform extraction of the aqueous extract.

To facilitate the extraction of caffeine from the fatty residue, the following procedure is suggested. About 10 g. of the dried, finely-ground coffee are extracted four times in a Soxhlet extractor with sodium-dried ethyl ether, which removes almost all the fat but only about 10 per cent. of the caffeine; the ethereal extract is evaporated to dryness, and the residue is extracted with boiling water in the usual way. As there is only a small proportion of the caffeine present in this extract, no great error can ensue through incomplete extraction with water. The de-fatted coffee in the Soxhlet thimble is moistened with about 5 ml. of water, after removal of the last traces of ether in a water-oven, and extracted with chloroform. The extract is then treated as before. As there is only a very small amount of fat present, the extraction of the caffeine is greatly facilitated. The combined aqueous extracts are extracted with chloroform, and the nitrogen of the impure caffeine is determined by the Kjeldahl method in the usual manner.

The results (Table II) are expressed as percentages of the dried coffee, the moisture-content being determined as with tea, by drying 1 to 2 g. of the finely-ground coffee at 100° C. for periods of 2, 4 and 6 hours; from the results obtained it was clear that 2 hours were sufficient.

TABLE II

COFFEES

Description	Mocha	Costa Rica	Malabar	Santos	Kenya	Mysore
Moisture, per cent.	6·8	7·4	6·5	6·8	6·8	6·9
Caffeine, per cent. (on dried coffee)						
Original Gorter method (fatty residue extracted with hot water)	0·96	1·10	1·32	0·92	—	—
	0·93	0·76	1·26	0·88	—	—
	0·89	—	1·32	0·82	—	—
	—	—	1·26	—	—	—
Modified Gorter method (fatty residue extracted by boiling with water)	1·05	1·21	1·33	0·99	1·09	1·28
	1·06	1·22	1·34	1·01	1·13	1·28
	1·10	1·23	1·35	1·02	1·14	1·25
Modified Gorter method (no $CHCl_3$ extn. of aqueous extract of fatty residue)	1·14	—	—	—	1·17	
Modified Gorter method (after separation of fat by extraction with dry ether)	—	—	—	0·99	—	—
Manganese, per cent. (on dried coffee)						
On broken beans	0·00131	0·00131	0·00181	0·00175	0·00324	0·00174
	0·00131	0·00132	0·00186	0·00176	0·00319	0·00173
	0·00129	0·00133	0·00186	0·00176	0·00318	0·00171
Finely-ground powder ..	0·00137	0·00149	0·00181	0·00187	—	0·00171
	0·00147	0·00150	0·00183	0·00186	—	—
	0·00149	0·00151	0·00184	0·00184	—	—
	0·00152	0·00151	0·00186	0·00183	—	—
On de-caffeinated powder ..	0·00140	0·00148	0·00178	—		
	—	0·00149	—	—		

The results for caffeine and manganese showed that there is a general tendency towards an inverse relationship between the manganese and caffeine contents of teas. No such relationship, however, exists with coffee, for which the caffeine-contents are relatively constant. It is worthy of note that African teas have, in general, a higher manganese-content than Indian. The sample of Kenya coffee had also a relatively high manganese-content.

We wish to express our thanks to Mr. A. A. Eldridge for helpful advice, and to Messrs. J. Lyons & Co. (per Dr. L. H. Lampitt), to Messrs. Gow, Wilson and Stanton, and to the Director of the Imperial Institute for supplying samples of teas and coffees.

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Observations on the Use of Potassium Chromate as Indicator for the Titration of Chlorides with Silver Nitrate

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MOHR'S original method for the determination of chlorides with silver nitrate has been the subject of numerous investigations, and, although the method is perhaps less widely used at the present time than formerly, on account of the rapidly extending use of adsorption indicators, it is still a standard method of analysis and likely to remain so for many years to come. Modern investigations on Mohr's method have been chiefly concerned with two factors, namely, the quantity of indicator which should be used in order to work the method with the maximum degree of accuracy, and the extent of the permissible deviations from strict neutrality of the solution.

In the older literature considerably varied quantities of potassium chromate were recommended for determining the end-point, but perhaps the most generally used quantity was of the order of 1 ml. of a one per cent. solution for a total volume of 100 ml. of liquid when solutions of $N/10$ concentration were analysed. Kolthoff,[1] having regard to the ionic products of silver chloride and silver chromate, recommended 1 ml. of a 1/3rd molar solution of potassium chromate per 100 ml. of liquid, corresponding to a chromate ion concentration of $3{\cdot}3 \times 10^{-3}$ molar. Van Urk,[2] as the result of similar reasoning, concluded that the minimum chromate ion concentration should be $0{\cdot}7 \times 10^{-3}$ molar and that the maximum concentration should not exceed 15×10^{-3} molar. It will be noted that van Urk's minimum concentration exceeds that which would be given by 1 ml. of a one per cent. solution of potassium chromate per 100 ml. of solution, the latter giving a chromate ion concentration of $0{\cdot}5 \times 10^{-3}$ molar.

Acid solutions of chlorides are most usually neutralised with calcium carbonate when Mohr's method is employed. Kolthoff (*loc. cit.*) investigated the limits of acidity which he considered permissible for accuracy. In his text-book[3] he summarised the best conditions for working the process, recommending the use of 1 to 2 ml. of a 5 per cent. solution of potassium chromate per 100 ml. of final volume of liquid, and giving the limits of the *p*H value of the solution as between

6·5 and 10·5. Acid solutions should be brought to this reaction by the use of borax or sodium bicarbonate. It may be added that Doughty[4] carried out a few experiments on the titration of acid solutions of chlorides which were buffered with sodium acetate to a *p*H value of 5·5, and he stated that accurate results were obtainable under these conditions.

Although much attention has been given to the concentration of the indicator and the relative acidity of the solution, very few, if any, writers have made any remarks on the alkaline properties of the indicator itself. Potassium chromate in solution is sufficiently hydrolysed to show a definitely alkaline reaction. Numerous investigations have been made, by physical methods, on the properties of solutions of chromates, of which mention may be made of Britton's experiments on the electrometric titration of chromic acid[5] and on the precipitation of basic chromates.[6] In this second paper the *p*H of potassium chromate in $M/100$ concentration is stated to be 9·25. It follows that the addition of potassium chromate to any chloride solution within certain limits of acidity will necessarily diminish its hydrogen ion concentration. The amount of change due to the quantity of indicator suitable for purposes of titration may be of the order of 1 to 2 *p*H units. If the limits of acidity of a chloride solution that can be titrated with accuracy by Mohr's method are to be clearly defined, either the indicator must be adjusted to *p*H 7 before it is added to the solution, or the *p*H of the solution containing the indicator must be determined before the titration is carried out. Solutions of potassium chromate can be adjusted to *p*H 7 by careful dilution with nitric acid, or, alternatively, with a solution of potassium dichromate. A solution of a mixture of potassium chromate and potassium dichromate has considerable buffering properties, as may be seen by a study of Britton's titration curves (*loc. cit.*).

There appears to be an impression among many chemists that ammonium chloride should not be determined by Mohr's method, but that Volhard's process should be used. This idea seems to be based partly upon the slight acid hydrolysis of the salt, and partly upon the influence of ammonium salts on the solubility of silver chromate. The *p*H of solutions of ammonium chloride of suitable concentration for volumetric determination is usually about 5. As regards the influence of ammonium salts on Mohr's process, Kolthoff (*loc. cit.*[3]) remarks that pure ammonium salts of strong acids are without influence upon the accuracy of the method, provided that the *p*H of the solution under these conditions is maintained within the limits of 6·5 and 7·2. At lower hydrogen ion concentrations ammonia is liberated, with disastrous effects on the accuracy of the process. It was primarily with the object of ascertaining the quantitative effects of acidity and of the presence of ammonium salts on Mohr's method that the experiments described in this paper were carried out. Some experiments were also made on the titration by Mohr's method of hydrochloric acid neutralised with calcium carbonate, with the object of effecting a comparison with results obtained by direct quantitative neutralisation with sodium carbonate.

EXPERIMENTAL

EFFECT OF ACIDITY ON MOHR'S PROCESS.—Titrations of potassium chloride with silver nitrate were carried out in the following way:—A weighed quantity of silver nitrate, slightly in defect of the amount of potassium chloride solution to be added, was dissolved in 25 ml. of CO_2-free water, and a measured volume of $N/100$ nitric acid was added. Then 63·74 ml. of approximately $N/10$ potassium chloride solution were added from a Stas pipette, followed by 2 ml. of a 1·5 per cent. potassium chromate solution which had been previously adjusted to *p*H 7·0 by addition of nitric acid. The titration was then completed by running in $N/20$ silver nitrate solution from a burette. The *p*H values were determined with the aid of a Lovibond comparator, solutions prepared in a precisely similar manner but with omission of the silver nitrate being used.

The results, given in Table I, are expressed in the form of weight of silver nitrate required for 63·74 ml. of potassium chloride solution. The figures given for solutions in the neighbourhood of neutrality are the average of several titrations, with a maximum deviation from the average of less than 1 part per 1000; at the higher acidities the plotted results showed that duplication was unnecessary. The first result recorded was obtained with unneutralised indicator of the same concentration, and the alkalinity is due to hydrolysis of the potassium chromate. Below *p*H 3·8 no satisfactory end-point was obtainable.

The effect of increasing acidity on the titration figures is seen more clearly from a graph, in which *p*H values are plotted against weights of silver nitrate.

TABLE I

*p*H of solution	Weight of silver nitrate required g.
7·8	1·0761
7·0	1·0763
6·2	1·0784
5·4	1·0797
5·0	1·0826
4·2	1·0941
3·8	1·1182
3·4	—

These results may be compared with the calculated quantity of silver nitrate and with the results of titrations in which phenosafranine was used as adsorption indicator.

Calculated weight of $AgNO_3$ = 1·0804*; average result with phenosafranine = 1·0754.

TITRATION OF AMMONIUM CHLORIDE, AND EFFECT OF EXCESS OF AMMONIUM SALTS.—These titrations were carried out in a manner similar to those previously described for potassium chloride, but with the use of approximately $N/10$ ammonium chloride solution (in quantities of 63·74 ml., measured from a Stas pipette). In order to study the effect of excess of ammonium salts, measured volumes of N solutions of ammonium nitrate or of ammonium acetate were added prior to completion of the titration with $N/20$ silver nitrate solution. The results recorded in Table II are in each instance the average of two or more determinations with a deviation from the average of less than 1 part per 1000.

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* A hypothetical figure, based on the assumption of 100 per cent. purity for both reactants.

TABLE II

	Conditions of experiment	pH of solution	Weight of silver nitrate required g.
1	Ammonium chloride solution, with no additional ammonium salts; unneutralised chromate indicator	6·9	1·1126
2	As (1), but with neutralised chromate	6·4	1·1126
3	As (1), but with addition of 1 mol. of NH_4NO_3 per mol. of NH_4Cl	6·8	1·1159
4	As (1), but with addition of 5 mols. NH_4NO_3 per mol. of NH_4Cl	6·6	1·1194
5	As (1), but with addition of 1 mol. ammonium acetate per mol. of NH_4Cl	6·9	1·1164
6	As (1), but with addition of 5 mols. of ammonium acetate per mol. of NH_4Cl	7·0	1·1319

These results may be compared with the calculated quantity of silver nitrate (100 per cent. purity of both reactants being assumed) and with titrations in which phenosafranine was used.

Calculated weight of $AgNO_3$ = 1·1088 g.*; average result with phenosafranine = 1·1118 g.

TITRATION OF HYDROCHLORIC ACID.—A weighed quantity of silver nitrate was dissolved in water, and 63·74 ml. of approximately $N/10$ hydrochloric acid were added, followed by 2 ml. of unneutralised chromate indicator. An excess of calcium carbonate was then added, and the liquid was shaken and allowed to stand for about two minutes. The pH of the solution at this stage varied between 5·8 and 6·4. The titration was completed with $N/20$ silver nitrate solution. The results of four determinations showed a maximum deviation from the average of just over 1 part per 1000. The figures in Table III show how the results compare with those obtained by other methods. For the sodium carbonate titrations, weighed quantities of the carbonate were treated with 2 × 63·74 ml. of the acid, and the titration was completed by running acid from a burette, bromophenol blue or methyl orange being used as indicator. This gave, for calculation, a titration figure of the order of 140 ml.

TABLE III

Method	Average result (g. of HCl per litre)
Mohr's	3·661
Phenosafranine ..	3·655
Sodium carbonate ..	3·653

SUMMARY AND CONCLUSIONS.—At the outset it may be noted that the quantity of potassium chromate that was used in our experiments would produce in the solutions a concentration of chromate ions of about $1·5 \times 10^{-3}$ molar. This particular concentration is well within the limits laid down by van Urk, and it may be doubted if any advantage is to be gained by working towards the upper limit set by him, on account of the very strong colour of the chromate ions. In any event the experimental error was less than one part in one thousand.

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* A hypothetical figure, based on the assumption of 100 per cent. purity for both reactants.

When neutral alkali chlorides are titrated by Mohr's method, highly accurate results are obtained, and, up to an acidity of *p*H 5·5, the error does not exceed 3 parts per thousand. At higher acid concentrations, however, the consumption of silver nitrate increases very appreciably. Thus at *p*H 3·8 the results are about 4 per cent. too high, and at *p*H 3·4 no definite end-point was obtainable.

In the titration of ammonium chloride by Mohr's process, the addition of the chromate indicator diminishes the acidity of the solution to a value well within the limits in which the maximum degree of accuracy of titration can be realised. The consumption of silver nitrate is only slightly higher than when phenosafranine is used as indicator, the difference being less than 1 part per thousand. That the presence of ammonium salts has a slight, but decided, effect upon the accuracy of the process is shown by the results obtained when ammonium nitrate was present. Thus when the molar ratio of ammonium nitrate to chloride was 5:1, the consumption of silver nitrate was increased by about 7 parts per thousand. The effect of ammonium salts of weak acids, such as ammonium acetate, is more pronounced. When the molar ratio of acetate to chloride was 5:1, the increase in consumption of silver nitrate was found to be nearly 2 per cent.

When hydrochloric acid is neutralised with calcium carbonate and then titrated by Mohr's method, the result is higher by about two parts per thousand than when the acid is determined by neutralisation with sodium carbonate. The *p*H value of hydrochloric acid treated in this way (*i.e.* with excess of calcium carbonate) is about 6, but it must be borne in mind that even the purest precipitated calcium carbonate commercially obtainable may contain about 0·1 per cent. of alkalis.

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THE CHEMICAL LABORATORY
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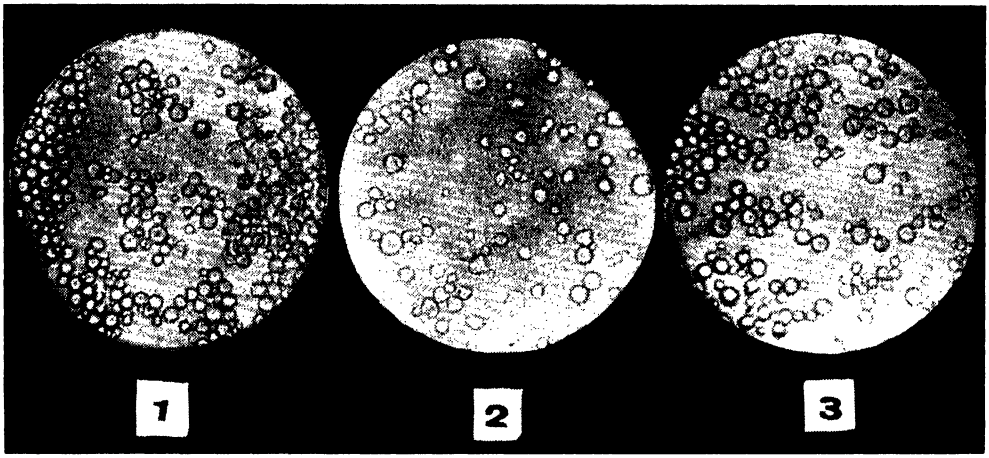

1 Tapioca starch 2 Sweet potato starch 3 Linseed starch
Magnification × 140

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE STARCH OF IMMATURE LINSEED

It is frequently necessary to examine linseed cake meals for adulterants, and, as the starch found in mature linseed is negligible, a positive iodine reaction is the prelude to a microscopical examination to identify the admixture.

For research purposes Mr. C. Robertson Louden grew linseed from imported seed in the wet summer of this year and handed to me, from his crop, some pods containing fully-grown but immature seeds. These seeds contained starch granules indistinguishable from those of tapioca starch, but slightly smaller than those of sweet potato starch.

As there appears to be no record of linseed starch in the literature, the accompanying photo-micrographs, taken by Mr. C. F. Waters in this laboratory, may be of interest.

In preliminary experiments Messrs. Louden and Antrobus have found that hydrocyanic acid is not evolved from linseed containing starch, but that as the starch is replaced by oil the seeds become cyanogenetic (*cf.* Analyst, 1939, 681).

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NOTE ON THE USE OF HYPOCHLORITE IN WATER ANALYSIS

R. Buydens (*Water Pollution Research*, 1936, **9** [No. 2], 51, par. 193) suggests that animal and vegetable organic matters in water may be differentiated by their relative action on potassium permanganate and sodium hypochlorite. This method, with slight modification, was adopted in the following determinations:

Permanganate Figure.—Ten ml. of $N/80$ potassium permanganate solution and 5 ml. of sulphuric acid (1 in 4) are added to 100 ml. of the water in a 500-ml. conical flask, the mixture is heated to boiling in 5 minutes, and boiling continued for another 10 minutes. After cooling, potassium iodide is added and the liquid is titrated with $N/250$ thiosulphate solution (1 g. of sodium thiosulphate per litre), starch being used as indicator.

Sodium Hypochlorite Figure.—Ten ml. of $N/10$ sodium hypochlorite solution are added to 100 ml. of the water in a 500-ml. conical flask, the mixture is heated to boiling, in 5 minutes, and boiling is continued for another 10 minutes. On cooling, 2 ml. of 10 per cent. potassium iodide solution and 10 ml. of strong hydrochloric acid are added, and the liquid is titrated with $N/40$ thiosulphate solution, α-naphthoflavone (0·1 per cent. in alcohol) being used as indicator.

In both titrations the results are expressed in parts of oxygen absorbed per 100,000 parts of water.

The liquids used in the experiments were made by adding vegetable and animal substances to tap water in such proportions as to give an oxygen absorbed

($KMnO_4$) figure in 4 hours at 80° F. of approximately 0·25 part per 100,000 for each solution.

	Permanganate absorbed in 4 hrs. at 80° F.	Permanganate absorbed in 10 mins. at b.p.	Hypochlorite absorbed in 10 mins. at b.p.	Ratio NaOCl:Permanganate (at b.p.)
Vegetable				
Peat	—	0·50	1·11	2·2 : 1
Leaf mould	0·28	0·48	0·92	1·9 : 1
Tea leaves	0·28	0·46	0·80	1·7 : 1
Pea	—	0·50	0·50	1·0 : 1
Animal				
Urine	0·26	0·52	4·4	8·4 : 1
Effluent	0·23	0·42	3·1	7·4 : 1

Thus the ratio between the two figures in presence of vegetable matter does not exceed 2, whereas that from animal sources lies between 5 and 8. These ratios obviously apply to drinking waters and should be particularly useful when an opinion has to be passed on waters of doubtful quality.

In order to give the process a more stringent test, an attempt was made to produce a liquid containing no animal matter, but having a ratio of albuminoid ammonia: oxygen absorbed suggestive of the presence of animal matter. This liquid was prepared by soaking bran with weak saline and filtering. The filtrate gave a positive biuret reaction, indicating the presence of protein derivatives. After adequate dilution it gave the following figures:

	Parts per 100,000
Albuminoid ammonia	0·045
Permanganate demand in 4 hours at 80° F.	0·14
,, ,, ,, 10 mins. at b.p.	0·73
Hypochlorite ,, ,, 10 ,, ,, ,, ...	0·75

The first two figures, interpreted in the usual manner, would lead one to assume the presence of animal matter, whereas consideration of the last two figures avoids such a fallacy.

F. Dixon
D. C. Jenkins

The County Laboratory
Stafford

August, 1939

Official Appointments

The Ministry of Agriculture and Fisheries has approved the following appointments:

H. C. L. Bloxam, F.I.C., as Agricultural Analyst for the County Boroughs of Gateshead, South Shields, Sunderland and Tynemouth, *vice* Dr. J. T. Dunn (deceased) (June 28th).

J. L. Wilson, M.Sc., F.I.C., as Deputy Agricultural Analyst for the County Borough of Burnley (June 28th).

Legal Note

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ADULTERATION OF "APPEAL-TO-COW" SAMPLES OF MILK

It may be of interest to other analysts to learn that milk may actually be watered under the eyes of the inspector. A case arose out of two samples purchased under the Food and Drugs Act in February, 1939. On the basis of the freezing-point depressions the informal and formal samples were certified to contain at least 3·5 and 2·3 per cent. of added water, respectively. Two days later, at the request of the farmer, the herd of ten cows was milked in the presence of two inspectors. The morning milk was found to be genuine, whilst the sample of evening milk contained 5·2 per cent. of added water. There was no question of a leaking cooler, and it was therefore suggested that I should accompany the two inspectors and take informal samples from each cow. The lighting conditions were poor, and as the inspector followed the farmer into the shed, he saw him pause, as if to adjust his apron. Then, as the farmer sat down to milk, he swung the pail, and the inspector heard a slopping sound, but before he could get to the farmer, milking had started, and although the pail had been dried previously, a considerable quantity of milky fluid was observed. The complete sample was calculated to contain 11·7 per cent. of added water. On the afternoon of the same day other samples were taken, and one was found to contain 9·4 per cent. of added water. The circumstances connected with the collection of this sample were highly suspicious, in that the farmer, while bending over the pail, was seized with a fit of coughing, and a gurgling sound, similar to that of liquid being poured from a bottle, was heard. Later a flat bottle was found concealed in the folds of the farmer's apron when it was removed. Further, the comparison of the analytical figures of this sample with those obtained by the chemists for the defence showed that by some means or other a genuine sample had been substituted and sent to them. This second portion was received in a sealed condition and no evidence of tampering could be seen in the bottle itself. On the following morning further samples from the cows alleged to have given the two watered samples were taken, and these were found to be genuine.

As the original sample contained only 2·3 per cent. of added water, as calculated from the Milk Regulations standard, it is probable that a caution might have been found sufficient, but the subsequent behaviour of the farmer resulted in a prosecution, and a fine of £50 with 10 guineas costs was imposed, two previous convictions having been recorded.

F. E. Needs

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF KINGSTON-UPON-HULL

Report of the Public Analyst for the Year 1938

Of the 2376 samples submitted under the Food and Drugs Act, 1376 were purchased formally.

Pork Dripping.—Four samples contained from 10 to 31 per cent. of water in the form of gravy, without label or declaration, in contravention of the local agreement with the Master Butchers' Association. The vendors were cautioned.

Ice-Cream.—The fats in two samples contained from 40 to 50 per cent. of vegetable fats. Hence it is desirable that any standard for the composition of ice-cream should take account of the fact that milk-fat is no longer the only source of fat in many of these confections.

The bacteriological examination of these products continued to cause misgiving. Of 56 samples examined, 40 were not satisfactory; more than half of these contained bacteria in excess of 500,000 per 1 ml., and also excessive numbers of *B. coli* (present in 0·1 ml.). The Medical Officer and I, in a joint report on ice-cream, recommended that standards and definitions for these products should be set up, and that consideration should also be given to the practicability of fixing bacteriological standards of purity. This report has been sent to the Ministry of Health.

Atmospheric Pollution Observations.—The results obtained during the year show that the amount of pollution, as judged by the deposit gauges, was practically stationary over the years 1936–1938. The average amount of solid matters deposited from the air (solid deposit and in solution in rain water) over the whole City in one year may be taken to be about 200 tons per square mile.

The daily average of sulphur dioxide in the air of the central area of the City is 0·03 volume per million during the summer months and 0·06 volume per million in winter. These figures may be compared with those of certain other areas for the year 1937–1938 (April to March): Hull, 0·06; Leicester, 0·10; London (Westminster), 0·14; Sheffield, 0·14 volume per million per day.

The amounts of sulphur gases (mg. of SO_3) per 100 sq. cm. of exposed surface of lead peroxide per day were as follows:—Maximum (January and December), 3·7; minimum (June), 1·4; average, 2·4.

The greatest amount of suspended impurities in the air was again recorded in November, when the figure was 51 mg. per 100 cubic metres. This result is in excess of the amounts found in the two previous years.

Ultra-Violet Light Observations.—The units of fading of a standard methylene blue solution recorded during the year varied from ¼ to 1½ as the daily average during each month. Comparative figures for Bridlington and Scarborough are:—Bridlington, ¼ to 1½; Scarborough, ½ to 2¾ units.

Chemical Evidence of Safe-breaking.—In this case material from the lock of the safe consisted of a brown fibrous cloth of wool and hair, with vari-coloured particles of plasticine, and the remains of an explosive substance containing ammonium nitrate and a nitrated compound of glycerol. This was incorporated in an absorbent material of the nature of oat-bran. Fabrics from a position near the area of explosion were torn to shreds and were charred or scorched by fire.

POISONING WITH PHENO-BARBITONE.—In a case of suicide pheno-barbitone was isolated in small quantities from the stomach contents (0·5 grain), liver (2·3 grains), and kidneys (0·3 grain). The pheno-barbitone crystals recovered had m.p. 173° C. Some 5-grain tablets examined in connection with this case consisted of the sodium compound of pheno-barbitone. ARNOLD R. TANKARD

WORCESTERSHIRE COUNTY COUNCIL

ANNUAL REPORT OF THE COUNTY ANALYST AND BACTERIOLOGIST

OF the 858 samples submitted under the Food and Drugs Act, 387 were purchased formally.

GUARANTEES OF FERTILISERS AND FEEDING STUFFS.—In my opinion, failure to give the statutory guarantee is, in most instances, more than a technical offence. Thus, in the guarantees for phosphatic fertilisers "phosphates" are guaranteed instead of phosphoric acid, and "ammonia" instead of nitrogen for nitrogenous fertilisers. Since 10 per cent. of phosphoric acid is equivalent to 21·8 per cent. of "phosphates" and 10 per cent. of nitrogen to 12·1 per cent. of ammonia, it is obvious that this kind of evasion of the Act gives the seller an advantage. Not all farmers are sufficiently versed in chemistry to watch for and appreciate these distinctions when buying fertilisers. These practices will continue until a prosecution is brought as a warning to vendors. Hitherto, however, the Minister of Agriculture has not been disposed to sanction such a course. H. E. MONK

Ministry of Health

SALE OF FOOD AND DRUGS

ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1938

THE number of samples of foods and drugs reported on by Public Analysts during 1938 was 150,576, a slight decrease on the number for the previous year (151,370) (*cf.* ANALYST, 1938, **63**, 816). Of these, 8433 or 5·7 per cent. were reported against.

PRESERVATIVES.—Contraventions of the Public Health Regulations were responsible for 430 adverse reports, of which 46 related to sausages. Table jellies contained benzoic acid, and barley, pickles and potted and other meats contained sulphur dioxide. Samples containing preservative in excess of permitted quantities included jam, sausages, dried fruits, beer, non-alcoholic wines and fruit juices. Boron preservative was present in cream, butter and sausages, in one sample of milk and in one of fresh meat.

MILK.—Of 80,025 samples (excluding 1494 "appeal-to-cow" samples with 620 reported as below standard), 6141 were reported against. In one case of successful prosecution a sample of milk contained 25 per cent. and in another the samples had up to 40·1 per cent. of added water. Also, a few samples contained dirt.

CONDENSED AND DRIED MILK.—Thirty samples of condensed and 4 of dried milk were reported against.

CREAM.—Of 27 samples of cream reported against, 11 contained boron preservative.

BUTTER AND MARGARINE.—Of 104 samples of butter reported against, 87 contained water in excess of 16 per cent., and one was also very rancid; 6 contained a large proportion of margarine, whilst 13 others consisted partly, and one wholly, of margarine; 3 contained boron preservative.

LARD AND OTHER FATS.—Eighteen samples of lard consisted wholly or partly of other fats, 3 samples contained water (1·4, 9·4 and 11 per cent. respectively), and one had excessive acidity. Most of the 35 samples of suet adversely reported on contained undeclared or excessive proportions of rice flour or other starchy matter, whilst 9 samples of dripping contained excess of water and 2 contained free fatty acids; one lard contained 30 per cent. of " nut " oil.

CHEESE.—A low fat-content was responsible for most of the 79 samples of cheese reported against. One sample of wrapped cheese was infested with acari and fungus, one was contaminated with crystals of sodium phosphate, one with crystals of lactose hydrate, and one contained 3·12 grains of tin per lb.

BREAD AND FLOUR.—Four samples of bread and 11 of flour were reported against. One flour contained 25 per cent. of potato starch and 2 samples of self-raising flour contained excess of sodium bicarbonate, whilst 2 ordinary flours were sold as self-raising flours.

JAM AND MARMALADE.—Many of the 165 samples reported against were deficient in fruit or soluble solids. Some samples of strawberry, of blackcurrant, and of raspberry jam were found to contain only 3 per cent. of the named fruit, and 63 samples contained excessive proportions of sulphur dioxide.

VINEGAR.—The chief trouble with the 152 samples of vinegar unfavourably reported on was a deficiency of acetic acid or a sale of artificial vinegar as "malt" or "table" vinegar.

SPIRITS AND BEER.—A deficiency of proof spirit was reported in 45 samples of whiskey, 32 of gin, 18 of rum and 8 of brandy, and one sample of whiskey was also stated to be mixed with wine, whilst a sample of rum contained 33·72 per cent. of ginger wine. Of 597 samples of beer, 66 were reported against, one sample for containing zinc and 62 for contamination with lead.

MISCELLANEOUS ARTICLES OF FOOD.—The 36,000 samples of other foods included a wide variety, of which only a few can be mentioned. Most of the 76 samples of canned fish reported against were condemned on account of contamination with tin, and tin was also responsible for the adverse reports on 41 samples of sugar, canned fruits, vegetables and soups, whilst lead was present in 19 samples of sardines and 10 of curry powder, and copper in a number of articles including sweets and canned tomato products. Zinc was present in ice-cream, one sample of dried apple rings and one of canned spinach, and arsenic in 2 samples of dried parsley, one of granulated gelatin and one of apples. Seventy-nine samples of chocolate rolls and other chocolate cakes were reported as deficient in cocoa matter, 56 of 69 samples sold as bread and butter proved to be bread and margarine, and 13 bread and a mixture of butter and margarine. One sample of cocoa contained 50 per cent. of cane sugar, one 6·75 per cent. of Epsom salts, one 1 per cent. of tapioca starch, and another starch and sand.

DRUGS.—Attention is called to the fact that several Food and Drug authorities took no samples of drugs during the year. Altogether 303 samples of drugs were found to be adulterated or not up to standard. Among these, a sulphur ointment contained no sulphur; iodine ointments and stainless iodine ointments were deficient in iodine; a sample sold as eucalyptus ointment contained 9 per cent. of methyl salicylate and no eucalyptus oil, and a sample of calomel ointment proved to be calamine ointment. Twenty-two samples of sweet spirit of nitre were reported against, mostly for deficiency of ethyl nitrite. Samples of ammoniated tincture of quinine were deficient in ammonia and/or quinine, and quinine cinnamon tablets were deficient in quinine sulphate. Bismuth and carbolic acid lozenges and aspirin tablets were unsatisfactory. Samples of camphorated oil, orange juice and halibut oil, sal volatile, magnesia, tincture of rhubarb, glycerin of borax (one sample consisted of 97 per cent. glycerin of phenol), linseed meal, blue pills, and hydrogen peroxide were reported against. A sample of paregoric consisted of orris root; two samples of ammoniated tincture of quinine were sold as dill water, and a nerve tonic consisted only of cane sugar with a small proportion of cocoa, barley flour and milk powder. Six medicated wines were unsatisfactory, as were also samples of Seidlitz powders, cream of tartar, Glauber's salt, stomach powders, lime water and syrup of figs. Three prescriptions were found to be unsatisfactorily dispensed. D. G. H.

FOOD AND DRUGS ACT, 1938

TABLES OF COMPARISON*

THESE tables show: (i) The mode in which earlier enactments are dealt with by the Act. (ii) The sections of the Act and corresponding provisions in earlier Acts.

Table I is headed: Statement of Provisions in repealed Acts and corresponding Provisions, if any.

Table II is headed: Statement of Provisions and corresponding Provisions in earlier Acts.

The earlier Acts cited are: Market and Fairs Clauses Act, 1847; Public Health Act, 1875; Milk and Dairies (Consolidation) Act, 1915; Milk and Dairies (Amendment) Act, 1922; Public Health (London) Act, 1936. Reference is also made to Standard Clauses, Revised Edition, 1937.

STATUTORY RULES AND ORDERS

1939 No. 840

FOOD AND DRUGS, ENGLAND

PUBLIC ANALYSTS

THE PUBLIC ANALYSTS REGULATIONS, 1939, DATED AUGUST 1, 1939, MADE BY THE MINISTER OF HEALTH UNDER SECTIONS 66 (2) AND 69 (3) OF THE FOOD AND DRUGS ACT, 1938 (1 & 2 GEO. 6. C. 56).

101745.

Whereas it is provided by subsection (2) of section 66 of the Food and Drugs Act, 1938, that no person shall be appointed a public analyst unless he possesses either the prescribed qualifications or such other qualifications as the Minister of Health may approve;

And whereas it is provided by subsection (3) of section 69 of the said Act that the public analyst shall analyse as soon as practicable any sample sent to him in pursuance of that section and give to the person by whom it was submitted a certificate in the prescribed form specifying the result of the analysis:

Now therefore the Minister of Health in exercise of the powers conferred upon him by the said sections and of all other powers enabling him in that behalf hereby makes the following regulations:—

1. These regulations may be cited as the Public Analysts Regulations, 1939, and shall come into operation on the first day of October, 1939.

2. The Interpretation Act, 1889,† applies to the interpretation of these regulations as it applies to the interpretation of an Act of Parliament.

3. A person shall not be qualified to be hereafter appointed as a public analyst under the Food and Drugs Act, 1938, unless either (*a*) he already holds an appointment as public analyst, or (*b*) he is the holder of the Diploma of Fellowship or

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* Pp. 18. To be obtained from H.M. Stationery Office, Kingsway, London, W.C.2. 1939. Price 3d. net.

† 52 & 53 Vict. c. 63.

Associateship of the Institute of Chemistry of Great Britain and Ireland and is also the holder of a certificate granted by that Institute after an examination conducted by them in the chemistry (including microscopy) of food, drugs and water.

4. The form set out in the schedule to these regulations is hereby prescribed as the form of certificate to be used by public analysts for the purpose of section 69 of the Food and Drugs Act, 1938.

SCHEDULE

FOOD AND DRUGS ACT, 1938

Form of Certificate of Public Analyst prescribed by the Minister of Health under Section 69 (3) *of The Food and Drugs Act,* 1938

To[1] ....

I, the undersigned, public analyst for the.., do hereby certify that I received on the...............day of................ 19...., from[2] ....(by registered post)[3], a sample submitted as a sample of.........................., for analysis which was marked[4]................... and weighed (or measured)[5]..

I further certify that I have analysed it, and as a result of my analysis I am of opinion that:—

it is a sample of..

and/or

the constituents of the sample included the following substances in proportions as under:—

Observations[6]

As witness my hand this............day of.. 19.
at...

A.B.

Notes.

[1] Here insert the name of the person submitting the sample for analysis.

[2] Here insert the name of the person delivering or sending the sample.

[3] Delete if inapplicable.

[4] Insert particulars of marking, *e.g.* date, number, etc.

[5] This may be left unanswered if the sample cannot be conveniently weighed or measured, or the weight or measurement is not material to the result of the analysis.

[6] Here the analyst may insert at his discretion his opinion whether the analysis indicates any addition, abstraction, or deficiency of any kind and whether the addition, abstraction or deficiency (if any) was for the purpose of rendering the article portable or palatable, or of preserving it, or of improving the appearance, or was unavoidable. He may also state whether the addition, abstraction or deficiency is in excess of what is ordinary, or otherwise, and whether it is or is not, injurious to health, and add any other observations he may wish to make. Where a sample of milk is found to be deficient both in milk fat and in other milk solids the analyst should indicate how much, if any, of the milk fat deficiency he considers to be due to abstraction, allowance being made for the effect of added water. In the case of a certificate regarding milk, or any other article liable to decomposition, the analyst should specially report whether in his opinion any change had taken place in the constitution of the sample that would interfere with the analysis.

Given under the official seal of the Minister of Health this first day of August, nineteen hundred and thirty-nine.

(L.S.) R. STANTON,
Assistant Secretary, Ministry of Health.

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT ON OBSERVATIONS IN THE YEAR ENDED MARCH 31ST, 1938*

THE 24th Report on the Investigation of Atmospheric Pollution surveys the researches carried out and the results obtained by the 88 bodies (80 of which are municipal authorities) co-operating with the Department in the measurement of atmospheric pollution. During the last ten years the organisation covered by this co-operative effort has grown considerably in size. In 1928 the co-operating bodies operated 79 deposit gauges; to-day this number has increased to 124. In 1928 there were 6 automatic filters, while to-day 16 of these instruments are now in use. The 11 sets of volumetric sulphur apparatus and the 54 sets of lead peroxide apparatus now in use are new since 1928, these methods for measuring sulphur pollution having been standardised in the course of the investigation.

A comparison of the figures obtained with deposit gauges for the year under review with the average deposit for the 5 years ended 1932 shows that, for tar, 57 per cent. of the stations where such a comparison is possible have a marked reduction in the deposit, whilst 30 per cent. show an increase. The figures for the deposit of total solids show that 55 per cent. of the stations indicated record a marked decrease, whilst only 9 per cent. show a marked increase. Except that a smaller percentage of the stations showed an increase in tar deposit in the year 1936–1937, all the figures for 1937–1938 are rather better than the similar figures for the preceding two years. This is fairly satisfactory, but it is pointed out that the results are affected by rainfall, which was below the average in 1937–1938.

FOG HAZE.—The results from the stations where apparatus is used for measuring impurities suspended in the atmosphere show that the lowest concentration of sooty matter was found at Cardiff, and the next lowest at Kew Observatory. As in previous years, Cardiff has shown an extraordinarily clean air. Of the places where observations were made throughout the winter, Greenwich, with 65 per cent., had the greatest number of days with heavy smoke haze. Next followed Stoke with 59 per cent., and then London (Victoria Street) with 54 per cent. Westminster City Hall had 43 per cent., Glasgow 19 per cent., and Coventry 3 per cent., whilst Cardiff recorded none.

It appears that there is a tendency for smoke fogs to occur more frequently on Mondays, Tuesdays and Wednesdays than on the other days in the week. The reason for this is not obvious.

LEICESTER SURVEY.—The most important work that the Department of Scientific and Industrial Research is now carrying out as part of the co-operative scheme is the survey of atmospheric pollution in and around Leicester. This has been in progress for over a year. The work consists of three sections: the routine measurement of pollution, the study and analysis of the observations made, and the designing and testing of new experimental instruments for the measurement of pollution. The immediate object of the survey is to obtain information on the general occurrence and distribution of the commonest forms of atmospheric pollution in a typical city, with a view to providing a general basis for the wider interpretation of existing and future observations made by the co-operating bodies. The observations are being made with some 43 instruments placed in 13 selected sites in and near Leicester. The instruments include all those specified by the Department's Atmospheric Pollution Research Department as standard.

FORMATION OF FOGS.—The Report contains a section by Dr. J. S. Owens explaining the way in which fogs are formed. In this country fogs are caused either by water droplets in the atmosphere or by smoke particles. The water droplets in a fog are only a few thousandths of a millimetre in diameter, and for this reason the sun, if visible, appears as a white disc. In a smoke fog particles are smaller, and the sun therefore appears red, because the smaller smoke particles scatter light of shorter wave-lengths but not light of the longer red wave-lengths.

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price: Report 2/- net; General Deposit Tables (issued separately) 4/6 net.

It appears essential in the formation of fog that the air should contain very small particles on which the water condenses. It is believed that sea salt is a prolific source of such particles and that nitrous and sulphuric acids are also important sources. The other essential condition for the formation of a water fog is that the temperature of the air must be cold enough for this condensation to take place. A high wind may prevent fog, but some wind is essential, so that the air can be cooled rapidly.

During condensation fogs there is nearly always, at a few hundred feet above the ground, a layer where the air is warmer than the air below. On a nearly calm day this layer of warm air forms a ceiling below which fog forms. The formation of this layer is an important link between a smoke fog and a water fog.

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY

CARBON BISULPHIDE VAPOUR

Erratum.—September issue, p. 675, l. 13, *for* "0·02" *read* "0·25 ml."

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST'S DEPARTMENT FOR THE YEAR 1938

The Report for 1938 by the Acting Government Analyst (Mr. A. C. Brooks) gives a detailed account of the work of the Laboratories of the Singapore and Penang Branches of the Department. In the Singapore Laboratory 20,647 samples and exhibits were examined for various Government departments, whilst in the Penang Laboratory the number was 5656.

Contamination of Liquor by Lead.—Lead was determined in 382 samples of Chinese samsoo. In 27 the lead-content exceeded 0·75 p.p.m., and the importers were warned; ten samples contained more than 1·5 p.p.m., and importation of the consignment was prohibited. The heaviest contamination encountered was 7·1 p.p.m., and a sample from a consignment, distilled in Singapore and previously found to contain only a negligible trace of lead, contained 4·4 p.p.m. The contamination was traced to the glaze of the pots in which the liquor was shipped and stored. Fortunately it was found that the glaze yielded only a limited amount of lead, and that new jars can probably be rendered safe for use by washing out the soluble lead with dilute acid.

Maturity of Brandy.—Legislation to extend to brandy the 3-years maturity requirement already in force for whiskey, was effected during the year. After January 1st, 1940, the importation of brandy will be prohibited unless it is officially certified to have been matured in wood for a period of not less than three years.

Perfumes and Spirit Duties.—In the Straits Settlements spirit duties are levied on Intoxicating Liquor and not on alcohol. This distinction exempts perfumes from payment of duty, provided that the alcohol used in their manufacture is sufficiently denatured with perfume oil to permit of its classification as "methylated spirits."

During the year the Customs Department submitted for classification 205 samples of perfume, mainly of local manufacture, prior to their release from bond. A quantitative estimation of the perfume oil in each sample was made, and 17 samples were classified as "not acceptable as perfume."

GHEE SUBSTITUTES.—There is a considerable local sale of imported refined and hardened vegetable and fish oils for use by the Mohammedan Indians as a substitute for ghee. In countries where such fats are used to replace lard they are sometimes known as "compound lard," and the use of this term on an invoice received in Penang caused a widespread rumour that these so-called vegetable oils were in fact derived from the pig, and there was much indignation among the users. Four samples of the fat were examined, but no evidence of the presence of fat of animal origin was found, and the importers and the public were reassured.

QUESTIONED DOCUMENTS.—An account book and a receipt book were submitted in a case in which the plaintiff alleged that an entry in the former had been made subsequent to the date stated, and that entries covering several months in the latter had been made within a few days of each other. No opinion could be expressed as to the relative ages of the entries, but it was found that the apparent newness of the account book entry was due to the use of a different kind of ink from that of the preceding and following entries, and that there had been at least three changes in the kind of ink used in the entries in the receipt book. In a case of alleged smuggling it was suggested that a pencil entry on one page of the ship's tally book had been made after the entry on the next page. A microscopical examination of the pencil impressions on both sides of the paper showed clearly that this was not possible.

POISONING CASES.—Of the 272 specimens of viscera, vomit, etc., examined, 181 were found to contain poison. The poisons detected included 78 of caustic soda, 16 of opium, 13 of tar oils, 13 of arsenic, 8 of tuba resin, 5 of cinnamon and clove oils, 4 of salicylic acid, 3 of formic acid, 2 of cyanide, 2 of mercury compounds, 2 of atropine, 2 of hydrochloric acid, and 1 each of various other deleterious substances.

In the Penang Laboratory 85 exhibits were examined and poisons were detected in 35. They included caustic soda or washing soda (17), arsenic (4), opium (3), alcohol (2), and one each of various other poisons.

A study of these results discloses, as in several previous years, the continued common use of caustic soda as a means of attempting suicide. To combat this, legislation has been introduced, making caustic soda a scheduled poison and thus rendering it more difficult to obtain. The most unusual case was that of a Chinese woman (a suicide) in whose alimentary tract was found not only morphine (probably taken as opium), but also 50 grams of coconut oil and copper sulphate equivalent to over 22 grams of the crystalline salt. The copper sulphate was probably administered as an emetic after the opium had been taken, and the coconut oil may have been intended as an antidote to one or both. After returning home the deceased tried to vomit, but failed, and shortly after became unconscious. The tongue and oesophagus were blackened, and the walls of the stomach and intestine were stained a vivid blue.

Face powders.—Four of six samples examined were satisfactory, but two contained much lead carbonate. Both of these came from a local factory, and one of them was directly associated with a case of lead poisoning.

BLOODSTAINS.—Blood was identified on 59 exhibits and demonstrated to be human in 51 of these. The blood on four exhibits—all connected with the same case—was found to be of a group other than that of the victim.

Blood from bugs.—In one case it was claimed by the defence that bloodstains on a garment were not connected with the alleged assault, but were produced by crushing bugs. The stains gave positive reactions for human blood, but experiments with bugs showed that, if these have battened on human beings, they yield a fluid which gives positive reactions for human blood, if crushed within a period of about 24 hours. Similarly, dog ticks were found to give a fluid giving the reactions for dog's blood for about the same period after removal from the dog. Grouping was attempted on the stains referred to above, but the experiments were not successful.

COUNTERFEIT COINING.—Two cases, involving the examination of 27 exhibits, were investigated. In the first case the exhibits comprised a fairly complete outfit for the moulding of 5 cent, 10 cent and 20 cent counterfeits, the metal employed being a tin-lead alloy probably derived from empty chandu tubes. By the examination of the moulding flaws it was possible to identify with certainty the moulds in which many of the counterfeits had been made. In the other case the "coins" submitted were counterfeits composed of tin with a trace of copper. Evidence was given that two of the coins, from different exhibits, had been made in the same mould as each other.

FRAUDULENT QUACKERY.—Two Chinese, posing as qualified doctors, were charged with fraud, and their pharmaceutical stock-in-trade (41 exhibits) was examined. Victims of the hoax described a trick in which a blood-red colour appearing on the patient's skin proved his urgent need of treatment. It was demonstrated in Court how, by the use of certain of the exhibits, the trick could be performed. The presence of phosphorus and arsenic among the "medicines" led to additional charges under the Poisons Ordinance.

Alkali, Etc., Works

REPORT OF THE CHIEF INSPECTOR FOR THE YEAR 1938*

THE seventy-fifth Annual Report on the operation of the Alkali, Etc., Works Regulation Act, 1906, and the Alkali, Etc., Works Orders, 1928 and 1935, is by the Chief Inspector, Mr. W. A. Damon. It states that the number of works registered in 1938 was 980, involving 1857 processes. The totals, compared with those of 1937, show an increase of 22 processes in the same number of works. There have, in particular, been decreases in the number of sulphuric acid, chemical manure and sulphate of ammonia processes, whilst increased numbers of gas liquor, chlorine and benzene processes have been recorded. The number of visits paid during the year was 4385.

In connection with the inspections, 2185 analyses were made of the chimney gases escaping into the atmosphere. The average of all the total acidity tests was 1·05 grains per cb. ft., as compared with 1·06 grains in 1937.

FUME EMISSION.—A number of complaints, apart from those of smoke, relating to works not registrable under the Alkali Act have been investigated. The unpleasant odour resulting from the boiling of linseed oil has been considerably reduced, but not altogether removed, by a system of intensive washing with sprays. Further progress has been made in the de-dusting of blast furnace gas; this is essential if local nuisances are to be avoided. In a complaint of fumes from the combustion of crude coke oven gas it was found that the waste gases contained hydrogen sulphide. By the admission of more air and with a better system of control the nuisance has been abated.

Emission of lead fumes.—Several complaints that fumes of lead had caused injury to cattle and injurious deposits on vegetation were traced to a works where battery residues were melted. As soon as the matter was brought to the firm's notice the plant was shut down, and additional dust recovery plant was installed. It is proposed to make an Order extending the schedule of registered works by creating a new class designated "Lead Works."

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* H.M. Stationery Office, York House, Kingway, London, W.C.2. 1939. Price 1/- net.

SULPHURIC ACID WORKS.—The production of sulphuric acid in England and Wales in 1938 was 821,000 tons, calculated as monohydrate. This represents a decrease of 103,000 compared with the production in 1937. The low production has made it easy to operate, with an escape within the prescribed limit (4·0 grains as SO_3 per cb. ft.), and only six infractions have been noted. The average escape from contact plants tested was 3·30 grains, a figure very slightly less than last year, but yet high compared with that from chamber plants. Reasonably good conditions have been maintained in concentration plants, the average escape being 0·54 grain compared with 0·70 grain in 1937.

CHEMICAL MANURE WORKS.—The average escape of acid gas (0·057 grain per cb. ft., expressed as the SO_3 equivalent of hydrofluosilicic acid) from chemical manure works was substantially the same as the previous year. Where new scrubbing plant is contemplated it should be borne in mind that it is important that there should be early cooling and wetting of gases followed by adequate delay to allow time for the decomposition of the silicon tetrafluoride to be completed.

ALKALI AND COPPER (WET PROCESS) WORKS.—In 1938 the amount of salt decomposed in the salt cake process was 52,880 tons, and in the wet copper process 5160 tons. The average of tests to determine the escape of hydrochloric acid in this class of work showed 0·074 grain per cb. ft., as compared with 0·077 grain per cb. ft. in the previous year.

CEMENT PRODUCTION.—At the end of 1938 there were 121 rotary kilns in England and Wales with a combined capacity of 1158 tons of cement clinker per hour. There is satisfactory progress to record in the installation of dust arrestment plant. At the end of 1938 the proportion of the total capacity produced in kilns fitted with electrical precipitators was 47·2 per cent. With a suitable arrangement of chains a reduction of dust emission to about 0·5 grain per cb. ft. (at 15° C.) can be achieved. There is no reason why the erection of any new plant should be permitted unless guarantees can be given that the dust emission will be suitably dealt with.

AMMONIA PRODUCTS.—The total output of ammonia products in England and Wales was 677,200 tons expressed as sulphate (25·75 per cent. of NH_3). The production of concentrated liquor has continued to rise. Of 81 coke-oven installations in England and Wales, 35 practise indirect ammonia recovery. Many of the responsible officials at coke ovens where shock cooling (and recirculation) is employed admit that the practice does give rise to offence, and many attempts are being made to overcome the difficulty.

ACCIDENTS AT CHLORINE-USING PLANTS.—In a bleaching powder works an escape of chlorine was detected. It was found to be due to a broken distributor plate in one of the scrubbing towers. In another works chlorine is passed into a batch of caustic soda so as to be entirely absorbed, with the production of sodium hypochlorite. An accident occurred in these works owing to an obstruction in the valve, which resulted in an accelerated flow of gas such that some passed through the absorber. A man in the vicinity was slightly gassed, and instructions have now been given that an attendant must always be on the spot while the process is in operation.

VISCOSE WASTE GASES.—A series of tests has been made to determine the effect of chlorine on waste gases from the spinning of viscose, and a definite reduction in hydrogen sulphide has been found to result. The plan of dosing the gases with a small quantity of chlorine is used at many works; it is found to be a palliative, but by no means a complete cure. At one works the gases are being scrubbed with caustic soda, and at another the gases are drawn off from the machines and burned at the boilers. It has not yet been found possible, however, to burn the whole of the gases.

Carbon Bisulphide.—The conditions accompanying the manufacture of carbon bisulphide have improved, but the possibilities are by no means exhausted. The "dropping" of retorts into open barrows, with subsequent quenching, causes much fume, and an enclosed receptacle has recently been devised which should render the operation much less offensive. Redistillation of carbon bisulphide has also been the cause of offensive odour on many occasions when steaming has been unduly heavy and the seals have in consequence been blown.

Registered Processes in Scotland.—The number of works in Scotland registered under the Act was 92, in which 161 scheduled processes were operated. During the year, 216 visits of inspection were made and 105 chemical tests were carried out; 316 visits were also made to places not registered under the Act. Production in Scottish chemical industries decreased slightly, but remained on a satisfactory level. The diminution in output was most apparent in the coking industry. Tar distilled and sulphate of ammonia produced in coke-oven plants decreased by over 10 per cent.

Royal Sanitary Institute

ANNUAL CONGRESS

The Annual Congress of the Royal Sanitary Institute was held at Scarborough from July 3rd to 7th. The Society was represented by Mr. Arnold R. Tankard, to whom we are indebted for the following notes on the proceedings.

The Inaugural Meeting was addressed by Lord Harewood, who, in an interesting Presidential Address, laid stress upon the importance of atmospheric pollution and its abatement.

At a meeting of the Sanitary Inspectors' session on Atmospheric Pollution there was an informative and valuable discussion. In the course of this, Mr. Tankard pointed out that most urban areas were more concerned with domestic than with industrial smoke, and that without some restrictive legislation it was much more difficult to remedy the former than the latter.

In the discussion on Clean Milk Production (Veterinary Hygiene session), Mr. Tankard put forward the view that the present bacteriological standards for graded milks were working well and were reasonable if somewhat lenient, but that more than half the milk supplies (liquid milk) were not subjected to any such standards or control, and that some criterion of bacterial purity should also be applied to these supplies, as they were largely consumed by the greater part of the population.

On the chemical side, Mr. Tankard directed attention to the fact that this Society had, through a specially appointed Committee, given special attention to dirty milk, and had devised a method for determining the amount of dirt in milk and for ascertaining its characteristics. He suggested that, as the Milk and Dairies Order required a standard of cleanliness, the standard for dirt in milk suggested by the Society should be given statutory authority.

British Standards Institution

THE following new British Standard Specification has been issued*:

No. 868—1939. COD OIL FOR SULPHONATION PURPOSES.

This Specification is intended to include the technical provisions necessary for the supply of the product referred to, but does not purport to include all the necessary provisions of a contract. It does not apply to materials which are intended for medicinal use and are included in the British Pharmacopoeia.

DESCRIPTION.—Cod Oil for Sulphonation Purposes shall be the oil obtained mainly, if not entirely, from the liver of the cod, *Gadus morrhua* Linn. and other species of the family *Gadidae*. The oil may contain a small proportion of the oil obtained from the livers of other fish commonly caught in association with cod.

The oil shall be an orange to dark red liquid, and shall be free from foreign matter.

SPECIFIC GRAVITY AND DENSITY.—The sp.gr. at 15·5°/15·5° C. shall be not lower than 0·920 nor higher than 0·930. The density, or weight in air, at 15·5° C. of unit volume (1 ml.) shall be not lower than 0·918 nor higher than 0·928.

IODINE VALUE.—This shall be not lower than 145 nor higher than 178, when determined by the method specified (Wijs method).

SAPONIFICATION VALUE.—To be not lower than 180 nor higher than 190, when determined by the specified method.

ACIDITY.—The oil shall be free from mineral and added organic acids. The acidity, as determined by a method specified in an appendix, shall be agreed between Purchaser and Vendor.

UNSAPONIFIABLE MATTER.—The oil shall not contain more than 3 per cent. of unsaponifiable matter when determined by the specified method (Society of Public Analysts' method).

COLD TEST.—The congealing point, as determined by the following method, shall be agreed between Purchaser and Vendor:

Warm the oil to 30° C. and allow it to cool to 20° C. Fill a test-tube (18 mm. in diameter) to a height of about 30 mm. with the oil. Then draw out the tube and seal, or cork tightly, cut off the cork level with the top and coat suitably to exclude moisture.

Expose the tube containing the oil at 0° C. (or such other temperature as agreed between Purchaser and Vendor) for 24 hours. There shall be no deposit of stearine and the oil shall be fluid. The tube shall be kept in a vertical position during the test.

SAMPLING AND SIZE OF SAMPLE.—Representative samples, each measuring not less than 400 ml. (approx. ¾ pint) shall be, wherever possible, taken in triplicate from original containers or from the bulk, and shall be packed in clean, dry, air-tight, non-absorbent containers (preferably of glass). The containers shall be of such size that they are nearly filled by the sample. Each sample container so filled shall be marked with full details and date of sampling.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Separation of Sugars by the Chromatographic Adsorption of their Coloured Esters. I. Separation of Glucose and Fructose. W. S. Reich. (*Biochem. J.*, 1939, **33**, 1000–1004.)—When esterified with azobenzene-*p*-benzene-sulphonyl chloride or azobenzene-*p*-benzoyl chloride, sugars yield coloured esters that are readily separated by chromatographic adsorption. Brockmann alumina can be employed for this purpose, but the esters are eluted more completely from columns of silica (pure precip. B.D.H.). The separated ester yields the sugar itself on hydrolysis, and azobenzene-*p*-benzoyl esters are hydrolysed more easily than the sulphonyl esters, and are preferred for this reason. Azobenzene-*p*-benzoic acid is prepared by the condensation of *p*-aminobenzoic acid with nitrosobenzene in alcoholic acetic acid solution, and is converted into its acid chloride by treatment with thionyl chloride in benzene solution. Esterification of glucose or fructose,

* Publications Department, 28 Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

with formation of penta-azobenzene-*p*-benzoyl-glucose or -fructose, was effected by adding a mixture of the acid chloride and pyridine, cooled to −20° C., to the sugar, and allowing the mixture to stand for several days at 12° C. The excess of reagent was converted into the methyl ester by the addition of excess of methyl alcohol, and the precipitated sugar ester was filtered off and washed with ethyl alcohol. Equal weights of the glucose ester and fructose ester thus prepared were dissolved in chloroform, and the solution was diluted with 2 volumes of benzene and 2 volumes of petroleum spirit. The mixture was filtered through a column of silica (pure precip. B.D.H.) prepared from a suspension in a 1 : 3 mixture of benzene and petroleum spirit (b.p. 60–80° C.). After the addition of all the ester solution, the column consisted of two red zones separated by an orange zone. It was then developed by washing with a large volume of the mixture (1 : 3) of benzene and petroleum spirit. The dark orange zone that had thereby formed at the top of the column yielded almost pure fructose ester when eluted with a mixture of methyl alcohol and chloroform (1 : 4), whilst a second dark orange zone, separated from the first by a broad colourless zone containing one narrow orange ring, yielded almost pure glucose ester on elution. Thus a very satisfactory separation was obtained by one chromatographic adsorption. F. A. R.

Seed Fats of *Salvadora oleoides* and *Salvadora persica*. B. G. Gunde and T. P. Hilditch. (*J. Chem. Soc.*, **1939**, 1015–1016.)—*Salvadora oleoides* and *Salvadora persica* (Indian names, jhal and pilu, respectively) *N.O. Salvadoraceae*, are small wild Indian shrubs with currant-like fruits and yellow seeds resembling those of mustard. The fruit-coats contained no fat but, on extraction with acetone, yielded about 1 per cent. of resinous material. The seeds constituted about 44 to 46 per cent. of the fruit, and the average weight of 100 seeds was 3·2 g. The seeds of (*a*) *Salvadora oleoides* and (*b*) *S. persica* yielded to petroleum spirit: (*a*) 41·0 and (*b*) 39·3 per cent., of pale yellow solid fats with the following characteristics:—saponification equiv., (*a*) 240·6, (*b*) 243·1; iodine value, (*a*) 5·5, (*b*) 6·1; acid value, (*a*) 1·0, (*b*) 2·2; unsaponifiable matter, (*a*) 0·7, (*b*) 0·8 per cent. The fatty acids had iodine value, (*a*) 5·0, (*b*) 5·5, and mean molecular weight, (*a*) 226·2, (*b*) 228·6. The mixed fatty acids of each fat were converted into methyl esters, which were fractionally distilled at 0·1 mm. through an electrically heated and packed column, and the fractions were analysed. Certain fractions were also examined quantitatively, and from the data obtained the composition (in per cent. mol.) of the acids was calculated to be:—decoic, (*a*) 2·0, (*b*) 1·3; lauric, (*a*) 24·1, (*b*) 22·3; myristic, (*a*) 52·7, (*b*) 54·6; palmitic, (*a*) 16·8, (*b*) 17·4; oleic, (*a*) 4·4, (*b*) 4·4. The data given differ considerably from those of Patel *et al.* (*J. Ind. Inst. Sci.*, **1926**, 9a, 117). D. G. H.

Rice Bran as a Raw Material of Oil. T. Hidaka. (*J. Soc. Chem. Ind. Japan*, **1939**, 42, 219–220B.)—The oils from fresh samples of rice bran taken throughout a year were extracted, and the free fatty acids were determined. The percentage rose steadily from 2·5 in the second month to 7·7 per cent. in the eleventh month. Rice brans from rice intended for food and from rice for saki, from both horizontal and vertical cleaning mills, were analysed. The two types of bran varied but little, but the horizontal mill produced a bran poor in starch (average 13·95 per cent.) and rich in oil (20·38 per cent.), whilst the bran from the vertical mill was rich in starch (average 24·03 per cent.) and poor in oil (15·21 per cent.). Examination of samples of bran taken during cleaning operations showed that the free fatty acids in the oil decrease with the progress of cleaning, *e.g.* from 4·45 per cent. at the beginning to 1·42 at the end. Rice bran from a horizontal cleaning mill contained 11·0 per cent. of moisture and 20·0 per cent. of oil, and yielded 14 per cent. of oil and 80 per cent. of press-cake containing 8·0 per cent. of moisture and 8 per cent. of oil. The average percentage composition of the rice-bran cake on the market in 1938 was:—moisture, 8·0; oil, 8·7; starch, 18·0; protein, 15·8; ash, 11·0; P_2O_5, 4·1. D. G. H.

"Hibiscus Flowers" and its Principal Constituent. C. Griebel. (*Z. Unters. Lebensm.*, 1939, **77**, 561–571.)—A preparation sold under the name of "Jericho Rose," and more frequently as "Hibiscus Flowers," was identified botanically as the calyx of *Hibiscus sabdariffa* L. (Natural Order: *Malvaceae*), a plant indigeneous to tropical America and cultivated in many tropical regions for the agreeably acid taste imparted by the sepals to beverages, sauces, jellies and sweet foods. The drug consists of the dark purple-red sepals which, when dried, are brittle and may be reduced to a violet-red powder. The principal diagnostic microscopical features are the thick-walled, pitted, flattened, plate-like cells of the epidermis (which has a striated cuticle) and hypodermis, the large round, elongated almost tubular mucilage spaces in the mesophyll especially near the vascular bundles, the calcium oxalate crystals (reaching 35μ in length), which are very numerous near the veins, the isolated, frequently broken, bristly and sometimes curved or coiled hairs, and the spiral and reticulated vessels of the midrib partly surrounded by thickened bast fibres. The drug is characterised by its colour, its peculiar brittleness and its acid taste. The residue obtained by evaporation of the alcoholic extract of the drug was dissolved in water and treated with lead acetate solution. The granular precipitate of the lead salt was washed, suspended in water and decomposed with hydrogen sulphide, and, after removal of lead sulphide, the filtrate was evaporated to dryness. The residue was a viscous mass which, when dried for several days in a desiccator, formed a mass of radiating crystals. The filtrate from the separation of the lead salt was treated with basic lead acetate in the same manner, and a yellowish mass was obtained which could not be crystallised. A qualitative examination of these two fractions revealed the presence of some malic acid and a considerable amount of an acid which resembled citric acid in some of its reactions (*e.g.* with Denigès' reagent), but differed from it in several other respects and had some reactions in common with malic and tartaric acids. Its m.p. (181° to 183° C.) and the m.p. of its *p*-nitrobenzyl and phenacyl esters (172° C. and 177° C., respectively) and its optical rotation (+11°) also showed that it was not identical with any of these acids. Ultimate analysis of its lead salt and its phenacyl ester gave results corresponding with the empirical formula $C_6H_6O_7$, and the presence of two carboxyl groups was indicated. Analysis of the lead and quinine salts (which contain one molecule of water of crystallisation removed by drying at 105° C., but not at 100° C.) gave an equivalent weight of 95. The high oxygen:hydrogen ratio suggested a derivative of citric acid, and the above-mentioned properties are consistent with the assumption that the compound is the lactone of hydroxycitric acid, which contains two asymmetric carbon atoms. This assumption is confirmed by the failure to form acid salts and by the fact that a solution of the compound made slightly alkaline to phenolphthalein becomes strongly acid again when warmed. The total titratable acid-content of the drug is 23 per cent., but this includes malic acid, another acid not yet investigated, and the red colouring matter which reacts with alkali. When the compound was isolated in the form of its lead salt, the yield was 13·6 per cent. When thin sections of the drug are immersed in hot lead acetate solution for an hour they turn bluish-green, and when mounted in chloral hydrate solution and examined microscopically are seen to be filled with needle-shaped crystals of the lead salt. The red anthocyanin colouring matter is extracted by 96 per cent. alcohol, and in aqueous solution gives greenish-blue and bluish grey-green precipitates with lead acetate and basic lead acetate solutions respectively. Mordanted wool fibre is not distinctly dyed. The sample contained about 8 per cent. of water and yielded 9·26 per cent. of ash containing much manganese. Per 100 g. of drug the aqueous extract (63·4 per cent.) yielded 7·6 g. of ash with alkalinity equivalent to 17·9 ml. $N/10$ Although titration of extracts with 2:6-dichlorophenol-indophenol indicated the presence of vitamin C, this could not be confirmed by other methods or by biological experiments, and this appears to be one of the rare instances in which this titration method leads to erroneous results. The drug appears to be a mild laxative and may be used for its agreeable thirst-quenching properties, but, apart from these, its therapeutic value is small, and the claims sometimes made for its action as a remedy in numerous illnesses are exaggerated and misleading. A. O. J.

Honeys Containing Octosan. W. Paul. (*Z. Unters. Lebensm.*, **1939**, **78**, 30–36.)—Octosan is a mixture of highly-acetylated sugars, principally the acetic ester of sucrose, and, owing to its very bitter taste, it is used as a denaturant. It can be fed to bees with the usual bee-foods (*cf.* Wahl, *Z. Vergl. Physiol. Chem.*, 1936, **24**, 116), and in presence of moisture is gradually decomposed into acetic acid and sucrose, so that the bitter effect, which is due to the undecomposed octosan, disappears gradually. Octosan is detected in bee-food sugar by extracting 20 g. of the sample in a Soxhlet apparatus with 50 ml. of dry ether, than removing the solvent by evaporation, and dissolving the residue in 5 ml. of 96 per cent. alcohol at 40° to 50° C. To this solution are added 2 ml. of conc. sulphuric acid and 2 drops of a 15 per cent. solution of α-naphthol in alcohol, when an intense red-violet colour shows the presence of octosan (Molisch reaction). In the quantitative method 50 g. of sample are extracted with 100 ml. of dry ether, the extract is evaporated, and the residue is dissolved in 20 ml. of methyl alcohol. This solution is mixed with 20 ml. of 0·1 N potassium hydroxide solution, and allowed to stand for 30 minutes, after which the excess of alkali is titrated with 0·1 N hydrochloric acid; then 1 ml. of 0·1 N KOH consumed ≡ 8·4 mg. of octosan. To a normal bee honey were added quantities of a solution of octosan in alcohol equivalent to 0·01 to 0·1 per cent. of octosan in the honey, and the taste was compared with that of untreated honey at intervals of two weeks at room-temperature. The bitter taste was no longer detectable after 6 and 14 weeks for the honeys containing

0·01 and 0·1 per cent. of octosan, respectively; the quantity of octosan normally used as a denaturant (0·075 per cent.) maintained its bitter effect for 12 weeks. There is reason to believe that the duration of the bitterness may vary according to the season of the year (see below). No appreciable influence on the sucrose-content of the honey, due to this treatment, could be detected. The detection of octosan in bee-honey is complicated by the fact that it undergoes progressive decomposition, forming sucrose, which may be already present in the honey, and acetic acid which, according to Nelson and Mottern (ANALYST, 1931, **56**, 403), also occurs naturally in honey. In the method suggested, however, 20 g. of honey are distilled with 30 g. of conc. phosphoric acid and 10 ml. of water in a 750-ml. round-bottomed flask, containing a little pumice and connected with a Liebig condenser, the end of the adaptor of which just touches the surface of 1 g. of dry calcium carbonate in a dish. Heating should be carried out cautiously to avoid foaming, and distillation is complete when no more liquid passes over and strong foaming starts in the flask. The contents of the dish are then dried at 120° C. and placed in an ignition tube, the outlet of which is directed on to a filter-paper that has been soaked in a fresh saturated solution of *o*-nitrobenzaldehyde in 2 *N* sodium hydroxide solution. When the powder is heated for 5 minutes at a low red heat, the calcium acetate present is decomposed into acetone, which produces a blue to blue-green colour on the yellow filter-paper (*cf.* Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, 2nd Ed., 1935, p. 408); addition of dilute hydrochloric acid to the paper destroys the yellow colour of the residual reagent, and leaves the blue of the indigo. This reaction gave negative results with 30 normal honeys and honeycombs of various types. A table shows the results obtained with 38 honeys from bees that had been fed on various diets, some containing octosans, for various periods and at various times of the year; these results are also correlated with the taste. Centrifuged honeys from bees that had been fed with sugar containing octosan in the autumn and pure sugar in the spring, gave little or no reaction for octosan and no bitter taste when examined in the following July or October. The use of an octosan sugar in both the autumn and spring resulted in a positive octosan reaction, although the honey was sweet. Honeycombs from bees that had been fed on octosan sugar in the winter, which were collected in March and tested in July, had a bitter taste and gave a positive octosan reaction. When an octosan sugar was used with the object of "over-feeding" the bee, so as to raise the yield of honey, the resulting honey had a positive octosan reaction.

J. G.

Standardisation of *Herba adonidis*. R. Koch. (*Deut. Apothztg.*, 1939, No. 33; *Pharm. Weekblad*, 1939, **76**, 1062–1063.)—The desirability of standardising the activity of this drug and preparations containing it is pointed out. It is used in place of *Digitalis*, especially in Russia, and in practice wide variations in activity have been observed corresponding with differences in the glucoside-contents. So far as is known, there are two *Adonis* glucosides: (i) adonivernoside, which is almost insoluble in water, readily soluble in chloroform or alcohol, sparingly soluble in ether, and insoluble in petroleum spirit; (ii) adonidoside, a yellow-white hygroscopic powder, which is readily soluble in water or alcohol, but insoluble in chloroform, ether or petroleum spirit. Since only the former has stimulating and diuretic properties, it is apparent that the activity of a preparation will depend on the process used. Merck's adonidin is a mixture of *Adonis* glucosides of high activity, which is readily soluble in water and gives with hydrochloric acid the red-violet colour characteristic of the insoluble adonivernoside. If Merck's adonidin is taken as standard, *Herba adonidis* is found to have an activity corresponding with an average glucoside-content (according to Heyl, Hart and Schmidt) of approximately 1 per cent. J. G.

Alkaloids of *Mitragyne speciosa*. I. Mitragynine. H. R. Ing and C. G. Raison. (*J. Chem. Soc.*, 1939, 986–990.)—The dried leaves of *Mitragyne speciosa* (Kratom of the natives) obtained from Siam (*cf.* ANALYST, 1934, **59**, 753) were extracted with 70 per cent. alcohol. On evaporation the extract left an aqueous layer and a resinous solid, each yielding two picrates: one, mitragynine picrate (m.p. about 220° C.) and the other with m.p. 123–127° C. Choline alone was isolated from the mother liquor of the former. Mitragynine has been given the formula $C_{22}H_{30}O_4N_2$ (or possibly $C_{22}H_{32}O_4N_2$), but no crystalline derivative could be obtained from the second picrate, which appeared to contain one or more alkaloids isomeric with mitragynine. The four oxygen atoms of mitragynine are distributed as two methoxyl and one carbomethoxy groups. It is a mono-acidic base yielding a mono-methiodide and cannot be acetylated, so that the second nitrogen atom is regarded as non-basic indole nitrogen. No hydrogen is absorbed by the base in contact with platinum or palladium, and the only permanganate oxidation products that could be recognised were oxalic and acetic acids. On alkaline hydrolysis a relatively stable intermediate substance, $C_{22}H_{30}O_4N_2$, *R*OH, appears to be formed, which on further action of the alkali yields the acid $C_{21}H_{28}O_4N_2$. No crystalline product resulted from selenium dehydrogenation, and distillation with zinc dust gave a base $C_{14}H_{14}ON_2$, which is possibly an *N*-methyl-methoxyharmine, and unidentified substances which gave indole colour reactions. D. G. H.

Origin of the Objectionable Odour that occurs on Burning Unfermented Tobacco which has been Harvested while in a State of Vitality. A. Wenusch. (*Z. Unters. Lebensm.*, 1939, **78**, 46–48.)—It has been found that the rate of drying of tobacco is influenced by the method of harvesting used, and that in certain circumstances an unpleasant odour is produced when the tobacco smoulders. In particular, this occurs when the principal rib of the leaf is split during harvesting, as this lowers the state of vitality of the leaf and drying occurs comparatively rapidly. Leaves gathered in this way were dried, finely powdered, and extracted in succession in a Soxhlet apparatus with ether, absolute alcohol and water. A test for odour on burning was made after each extraction, and the same unpleasant odour resulted in each instance; its intensity was increased by the extraction with water. These experiments eliminate chlorophyll as the source of the odour, and suggest that protein matter is mainly responsible. The residue was then heated with hot dilute hydrochloric acid (1:5) for 12 hours, when only 30 per cent. of the original weight of tobacco remained; the odour, however, was still apparent when the new residue was burned. Finally, this residue was treated with potassium hydroxide solution (1:20); only 7 per cent. of the tobacco then remained, and this was mainly cellulose, and when it burned the odour obtained was that of a burning cigarette paper and was free from the objectionable constituent. Confirmation that the odour is due to protein matter was obtained by digesting 5 g. of the powdered tobacco with 0·05 g. of trypsin for 24 hours at 30° C. in presence of 50 ml. of water and also of 4 per cent. ammonia. Comparison with control tests made with water and with the ammonia only, showed that the trypsin is necessary to remove the odour, and that it is particularly effective in presence of ammonia. It is considered that fermentation converts the proteins into a form in which they do not produce the undesirable odour when burned (*cf.* Wenusch, *id.*, 1937, **73**, 185; 1938, **76**, 41, 241, 433). J. G.

Biochemical

Colorimetric Method for the Estimation of Nicotinic Acid and Nicotinamide in Foodstuffs. H. Kringstad and T. Naess. (*Z. physiol. Chem.*, 1939, **260**, 108–118.)—Now that nicotinic acid (with its amide) has been established as the anti-pellagra factor, a method of estimating these substances chemically in foodstuffs is highly desirable, more especially as no satisfactory method of biological assay is at present available. There are two possible colorimetric methods—the first based on Vongerichte's dinitrochlorobenzene reaction, the second based on Koenig's reaction using cyanogen bromide and an aromatic amine. The second of these was selected for study, and the influence of various factors on the intensity of the colour produced was investigated. The optimum *p*H for both substances was found to be 6·1 to 6·5, but whereas the maximum colour was produced in 6 minutes with nicotinic acid, 23 minutes were required with the amide. The intensity of the colour also increased with increasing amounts of cyanogen bromide solution up to a maximum which was different for the two substances. Thus, when 0·35 ml. of the reagent was added to 10 ml. of a solution of the acid, two-thirds of the maximum colour developed, whereas a solution of the amide under similar conditions gave less than half this amount, thus making the difference between the acid and the amide more marked.

The material to be tested was minced and, after being thoroughly mixed with 2 to 3 times its volume of water, was heated for 1 hour on the steam-bath and filtered. The residue was extracted twice more, and the combined extracts were treated with sulphuric acid until the acidity was equivalent to 0·1 *N*. The liquid was then heated for 2 hours at 100° C. to liberate nicotinamide from the co-enzyme and the sulphuric acid was neutralised by addition of baryta and the barium sulphate filtered off. The filtrate was diluted to a suitable volume, and 20 ml. were made up to 25 ml. with phosphate buffer solution (17·60 g. of potassium dihydrogen phosphate and 6·67 g. of disodium phosphate were dissolved in water and the solution made up to 250 ml.), giving a *p*H of 6·3. Ten ml. of this solution, containing 1 to 50γ of nicotinamide, were transferred to the cell of a Pulfrich photometer and 4 drops of aniline solution (presumably saturated) followed by 0·35 ml.

of cyanogen bromide solution* were added. The other cell contained nicotinamide solution without added reagents. Filter S.47 (and later S.45) was used, the maximum colour developed was measured and the amount of nicotinamide present was calculated by reference to a standard curve. Another portion of the extract (100 ml.) was heated on the steam-bath with 15 g. of (hydrated) barium hydroxide for 2 hours, to hydrolyse the amide quantitatively to nicotinic acid. The solution was neutralised with sulphuric acid and centrifuged. The barium sulphate precipitate was washed with three 25-ml. portions of hot water, and the combined filtrate and washings were made up to volume. The measurement of the colour was carried out as for nicotinamide. Almost quantitative recovery of added nicotinic acid and nicotinamide was obtained by the method. The following are the most important results obtained for the nicotinic acid and amide contents of foodstuffs:

	Estimated as nicotinamide mg. per 100 g.	Estimated as nicotinic acid mg. per 100 g.
Beef	4·9	4·9
Pork	—	3·3
Ox-liver	15·5 to 18·7	15·5 to 20·0
Cod (muscle, roe or liver)	1·4 to 1·6	1·4 to 1·7
Salmon (preserved)	6·4	6·0
Herring	2·1	2·9
Potato	0·5	1·0
Wheat-bran	—	5·0
Rye	—	1·3
Wheat-germ	—	4·2
Maize	1·7	1·3
Brewers' yeast (dried)	—	45·5

These values agree well with such biological results as have so far been obtained.

F. A. R.

Estimation of Nicotine in Urine. A. C. Corcoran, O. M. Helmer and I. H. Page. (*J. Biol. Chem.*, 1939, **129**, 89–97.)—Two methods for the estimation of nicotine in urine were investigated. The first, depending on the formation of a precipitate of nicotine reineckate and measurement of the colour of its solution in diacetone, was found to be applicable to amounts of nicotine greater than 2·0 mg. The second, depending on Koenig's reaction with cyanogen bromide and a base, was found to be capable of detecting 0·05 mg. of nicotine.

Method 1.—A 24-hour urine sample preserved with chloroform is made alkaline with 5 ml. of 40 per cent. sodium hydroxide solution and extracted with ether in a continuous extractor for 36 to 48 hours, 15 ml. of 0·1 *N* hydrochloric acid being placed in the receiver. At the end of the extraction the ether is distilled from the extract, the residual aqueous solution is transferred to a 500-ml. Erlenmeyer flask, and the *p*H is adjusted to 3·0. The original receiver is rinsed with two or three 10-ml. portions of Sørensen's 0·15 *M* citrate buffer solution, *p*H 3·0, and the rinsings are poured into the Erlenmeyer flask. The solution is then steam-distilled for 50 to 60 minutes and the distillate is discarded, thus removing pyridine and homologues. After cooling, the solution is made alkaline to phenolphthalein and again steam-distilled for 50 to 60 minutes into a flask containing 15 ml. of 0·1 N hydrochloric acid, an adaptor dipping well below the surface of the acid being used. The acid is concentrated under reduced pressure to 3 to 5 ml., transferred to a 50-ml. beaker, and followed by four 5-ml. rinsings of water. The solution is evaporated on the steam-bath to about 1 ml. and transferred to a 15-ml. graduated centrifuge tube with the aid of three 1-ml. portions of water. The solution is made up to 5 ml. with water, 10 ml. of a freshly prepared, cold, saturated solution of Reinecke salt are added, the liquids are mixed, and the tube is allowed to stand at 2° to 3° C. for 3 hours. The precipitate is filtered off with the aid of a Pregl filter-tube, and washed with several 1-ml. portions of cold water until the washings are colourless. The filter-tube is then washed into a 10- or 25-ml. graduated flask with several 1-ml. portions of diacetone until all the reineckate has been extracted, after which the solution is made up to volume. Its colour is measured by means of a photoelectric colorimeter (filter No. 520), pure diacetone being used in the compensating tube. The nicotine-content is calculated from a calibration curve. The recovery of nicotine, added to 250-ml. portions of distilled water (no ether extraction or steam-distillation), was 100 per cent. The recovery of 2·0 mg. of nicotine, added to non-smoker's urine, was 85 to 92 per cent., but the colour equivalent of non-smoker's urine was 0·3 mg. per 24 hours.

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* Concentration not stated; presumably 4 to 5 per cent.—F.A.R.

Method 2.—A portion of urine containing about 0·2 mg. of nicotine is made alkaline to phenolphthalein with 40 per cent. sodium hydroxide solution and concentrated by distillation to a volume of 5 to 10 ml., the distillate being collected in, and below the surface of, 20 ml. of N hydrochloric acid. The distillate is concentrated on the steam-bath to 5 to 10 ml. and made alkaline to phenol red with N sodium hydroxide solution. The solution is then extracted with three 40-ml. portions of ether, and the combined ethereal extracts are distilled after addition of 5 ml. of N hydrochloric acid. To the residue so obtained 8 drops of 0·02 per cent. *o*-cresolphthalein solution are added, and the reaction of the solution is adjusted with 0·1 N sodium hydroxide solution and hydrochloric acid until the colour has just disappeared (approximately *p*H 8·2). The solution is transferred to a 25-ml. flask and made up to volume with 12 per cent. sodium acetate solution and water, so that the final solution contains 3 per cent. of sodium acetate. Five ml. of this solution are transferred to a colorimeter tube, and 2 ml. of cyanogen bromide solution are added. (This is prepared by dissolving 4 g. of sodium bromide, 3 g. of sodium bromate and 3 g. of sodium cyanide in 90 ml. of water, cooling the solution to 0° C. and slowly adding 10 ml. of 12 N sulphuric acid.) After being cooled in an ice-bath for 45 minutes the solution is treated dropwise with 4 ml. of alcoholic benzidine solution (50 mg. per 100 ml.), and the colour is measured 7 to 13 minutes afterwards at half-minute intervals, 3 per cent. sodium acetate solution being used in the compensating tube with filter No. 420. The nicotine-content is calculated from the maximum extinction observed by reference to a calibration curve. Recoveries of 87 to 100 per cent. of nicotine added in amounts of 0·20 to 0·40 mg. were obtained. The second method is the more convenient and accurate. F. A. R.

Determination of Chlorides in Biological Fluids by the Use of Adsorption Indicators. A. Saifer and J. Hughes. (*J. Biol. Chem.*, 1939, **129**, 273–281.)—To 0·2 ml. of urine in a Pyrex test-tube were added 3 drops of 3 per cent. hydrogen peroxide (chloride-free), and the tube was heated in a boiling water-bath for 2 minutes. Five ml. of 0·45 per cent. (hydrated) zinc sulphate solution and 1·0 ml. of 0·1 *N* sodium hydroxide solution were added, and the tube was heated in the water-bath for a further 3 minutes. After cooling, the contents were filtered (or centrifuged), and the filtrate and washings were transferred to a 25-ml. conical flask. Two drops of dichlorofluorescein indicator (0·05 per cent. solution in 50 per cent. alcohol) were added, and the solution was titrated with 0·02 *N* silver nitrate solution to the first definite pink colour that appeared throughout the solution. The results obtained by this method agreed very closely with results obtained by Caldwell and Moyer's modification (*Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 38) of the Volhard method and by Van Slyke's nitric acid digestion method (*J. Biol. Chem.*, 1923–24, **58**, 523). Albuminous urines also gave results in agreement with those obtained by the Van Slyke method. With the latter as standard, the maximum error was about 2 per cent., and the average less than 1 per cent.

Chloride determinations were also made by this method on zinc filtrates of blood serum or plasma. The latter (0·2 ml.) was pipetted into a Pyrex test-tube, and 1·0 ml. of 0·1 *N* sodium hydroxide solution was added, followed by 5·0 ml. of 0·45 per cent. zinc sulphate solution, drop by drop. The liquid was then heated in a boiling water-bath for 3 minutes, cooled, filtered, and titrated as described above. Whole blood zinc filtrates were similarly titrated. The average deviation of the method was ± 2 per cent. F. A. R.

Micro-estimation of Fluorine in Blood. H. Wulle. (*Z. physiol. Chem.*, 1939, **260**, 169–174.)—The method proposed by Kraft (*Z. physiol. Chem.*, 1937, **246**, 233) has been modified. The first stage, namely, the ashing of the blood serum, was found to be subject to a grave risk of error through loss of fluorine, and to avoid this, the following procedure was adopted. The serum was charred in a porcelain crucible, and the residue transferred to a gold crucible and finely powdered. A carefully regulated stream of oxygen was passed into the crucible, which was meanwhile gently ignited. Sintering of the ash, which should be quite colourless after an hour's heating, must be avoided. This method of ashing was found to be superior to ignition either with sodium peroxide or with potassium perchlorate. The second stage comprised the distillation of the ash with powdered glass (not siliceous earth, which adsorbs fluorine) and sulphuric acid at 135° to 140° C. in a current of steam, the fluosilicic acid that distilled being collected in sodium hydroxide solution. When more than 20γ of fluorine were present, distillation was incomplete, and it is recommended that three successive distillations should be carried out. The third and final stage consisted in the titration of the fluoride solution with the acid zirconium oxychloride-purpurin reagent of Kolthoff (*Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 118). It was found advantageous to dilute the purpurin solutions, as used by Kolthoff, with an equal volume of water and to make the fluoride solution neutral before titrating. Horse-blood serum was found to contain 80 to 90γ of fluorine per 100 ml. and human serum (70 analyses) from 35 to 145γ per 100 ml. F. A. R.

Occurrence of Free Vitamin A Alcohol in Fish Livers.—T. H. Mead. (*Pharm. J.*, 1939, **143**, 102–103.)—Fresh livers from the ling (*Molva molva, M. vulgaris* Day) were stored in solid carbon dioxide before the oil was extracted. The minced livers were then ground with sand and anhydrous sodium sulphate and extracted with cold peroxide-free ether. The ether was removed by distillation in nitrogen, and the oil was immediately heated for a short time at 100° C. in a high vacuum to remove traces of water and inactivate any hydrolytic enzymes. Two batches of such oil were subjected to molecular distillation, the apparatus and technique of Hickman being used. Of the total vitamin A present, 1·9 and 1·8 per cent., respectively, distilled at, or below, 150° C.; after allowance had been made for the overlapping of the elimination curves of vitamin A alcohol and vitamin A esters, it was concluded that not more than 1·0 per cent. of vitamin A alcohol was present in the first batch of oil and not more than 2·1 per cent. in the second batch. F. A. R.

Determination of Anti-neuritic Vitamin in Natural Materials. P. Meunier and C. Blancpain. (*Compt. rend.*, 1939, **208**, 768–770.)—The method depends on measurement of the colour developed by the reaction of the substance with diazotised sulphanilic acid alone and in presence of potassium ferricyanide. Vitamin B_1 gives a coloured product only in the absence of potassium ferricyanide, whilst other amino compounds which may accompany the vitamin, such as histidine, histamine, thiazol, and tyrosine, give colours which are not affected by the ferricyanide, enabling the vitamin to be determined by difference. Meunier's electrophotometric technique is employed (*Bull. Soc. Chim. Biol.*, 1937, **19**, 113). Into the photometric cell are introduced 2 drops of a 1 per cent. solution of sulphanilic acid in 10 per cent. hydrochloric acid and 4 ml. of Kinnersley and Peters' solution (*N*/2 sodium hydroxide solution containing 2·9 per cent. of sodium bicarbonate) to which has been added 0·3 per cent. of sodium nitrite. After a few seconds 1 ml. of the solution to be tested (*p*H 5 to 6 and containing 3 to 30γ of vitamin B_1) are added. Photometric readings are made (with the use of the green light-filter) exactly 30 seconds after the addition, and at 15-second intervals for a further minute. The process is repeated with a similar quantity of the solution to be tested to which has been added 0·1 per cent. of potassium ferricyanide. The photometric reading-time curve is plotted for both sets of readings: the difference between the readings (ordinates) gives a measure of the vitamin content. Tests were carried out with yeast extract. S. G. C.

Vitamin K from Alfalfa. P. Karrer and A. Geiger. (*Helv. Chim. Acta*, 1939, **22**, 945–948.)—Pure vitamin K_1 obtained from alfalfa is an oil, for which the name α-phylloquinone is proposed. Analysis and molecular-weight determination indicate a formula between $C_{30}H_{44-46}O_2$ and $C_{32}H_{48-50}O_2$. It is unstable to light, and possesses quinonoid properties, being reduced by zinc and acetic acid or by sodium hydrosulphite to a colourless hydroquinone that is readily re-oxidised by atmospheric oxygen to the original quinone. The vitamin can, in fact, be reduced potentiometrically with sodium hydrosulphite solution in 80 per cent. alcohol buffered with sodium acetate (0·02 *N*) and acetic acid (0·02 *N*). The titration is carried out at 25° C., and the titration-curve has a well-defined plateau corresponding with a molecular weight of 446. The redox potential is equal to +0·005 volt. In acetic acid solution, α-phylloquinone can be catalytically reduced, four molecules of hydrogen being taken up. By a reducing acetylation, a colourless hydroquinone acetate with an absorption maximum at 282$m\mu$ and a minimum at 250$m\mu$, is formed. F. A. R.

Colour Reactions in Vitamin K Concentrates. H. J. Almquist and A. A. Klose. (*J. Amer. Chem. Soc.*, **1939**, **61**, 1610–1611.)—The colour reaction first described by Dam, Karrer *et al.* (*Helv. Chim. Acta*, 1939, **22**, 310) affords an easy method of assessing the vitamin K activity of concentrates. A few mg. of the concentrate are dissolved in 1 to 2 ml. of methyl alcohol, and 1 ml. of sodium methylate solution (2 to 3 g. of sodium dissolved in 50 ml. of methyl alcohol) is added. When warmed for a few minutes, the mixture slowly develops a distinct purple colour if sufficient vitamin K is present and interfering pigments are absent. Soon the colour changes to a reddish-purple and finally to a reddish-brown. Carotenoid pigments can be extracted from the solution at this stage by means of petroleum spirit, leaving the reaction product in the methyl alcohol layer. The colour intensity of this solution showed a close correlation with the biological activity of the original concentrate. F. A. R.

Derivatives of Vitamins K_1 and K_2. S. B. Binkley, D. W. MacCorquodale, L. C. Cheney, S. A. Thayer, R. W. McKee, and E. A. Doisy. (*J. Amer. Chem. Soc.*, 1939, **61**, 1612–1613.)—Reductive acetylation of vitamin K_1 (from alfalfa) resulted in the formation of the diacetate of dihydro-vitamin K_1, which crystallised readily from petroleum spirit (b.p. 30° to 60° C.), or methyl alcohol, in fine white needles, m.p. 59° C. Analysis agreed with the composition $C_{36}H_{56}O_4$. The substance possessed marked vitamin K activity, and its absorption spectrum showed intense absorption at 230 $m\mu$, where $E^{1\%}_{1\,cm.}$ was 1250. The compound was not readily hydrolysed, but was converted into vitamin K_1 by treatment with methyl magnesium iodide, followed by shaking an ethereal solution of the product with air. The vitamin had the composition $C_{32}H_{48}O_2$. In a similar way vitamin K_2 (from putrefied fish meal) was converted into the diacetate of dihydro-vitamin K_2. This had m.p. 57° to 58° C. and the composition $C_{44}H_{60-62}O_4$. It also was biologically active and had an absorption spectrum very similar to that of the vitamin K_1 derivative. F. A. R.

Colour Reaction for Vitamin K. E. Fernholz, S. Ansbacher and M. L. Moore. (*J. Amer. Chem. Soc.*, **1939**, **61**, **1613**–1614.)—The colour reaction described by Dam *et al.* (*Helv. Chim. Acta*, **1939**, **22**, 310), and claimed by them to be characteristic of vitamin K is not a criterion for the presence of the vitamin. A concentrate having high biological activity and giving the colour reaction very strongly was chromatographed on a column of heat-activated calcium sulphate from petroleum spirit solution. The fraction eluted from the column gave an intense colour reaction, but was biologically inactive, whereas the filtrate gave only a slight darkening with the ethylate solution and contained all the biological activity of the original preparation. By repeated chromatographic adsorption, an apparently homogeneous substance was obtained, comparable in biological activity with the vitamin K_1 of McKee *et al.* (*J. Amer. Chem. Soc.*, **1939**, **61**, 1295). During the last stages of the isolation process, the sodium ethylate colour reaction became positive, but never reached the intensity of the inactive fraction previously separated. It is believed that the blue colour is due to readily formed decomposition products of vitamin K. F. A. R.

Organic

Separation of Mixtures of Dicarboxylic Acids. F. Rennkamp. (*Z. physiol. Chem.*, 1939, **260**, 276–278.)—Although the higher dicarboxylic acids, unlike the corresponding fatty acids, can generally be separated from one another by fractional crystallisation, the increasing importance of such acids in biological work makes it desirable to find a method of separation that can be used when a variety of other compounds are present in addition. A study was therefore made of the separation by distillation of the methyl esters of azelaic and sebacic acids. A mixture of known weights of the two acids was esterified with methyl alcohol and sulphuric acid, and the mixed ester (obtained in 97·6 per cent. yield) was distilled at 125° to 140° C. under a vacuum of 0·01 to 0·02 mm. Of the eleven fractions collected, the first two yielded pure azelaic acid on hydrolysis, and the last four yielded pure sebacic acid. The azelaic acid contents of the intermediate fractions (after hydrolysis) were calculated from their equivalent weights determined by titration with standard alkali. The total azelaic acid thus found was 38·24 per cent., as compared with 36·71 per cent. actually present. F. A. R.

Colorimetric Reaction for the Detection and Determination of Small Quantities of β-Naphthol. J. A. Gautier. (*J. Pharm. Chim.*, 1939, **30**, 70–76.)—Very small quantities of β-naphthol, of the order of 1 mg. or less, can be detected and determined by means of the pink or red colour produced when β-naphthol reacts with nitrous acid. The reaction is not given by α-naphthol or β-naphthyl ethers.

Detection of β-Naphthol.—When 1 ml. of a solution of β-naphthol in 30 per cent. alcohol, the concentration of the solution being between $M/20$ (0·72 g. in 100 ml.) and $M/1000$ (0·0144 g. in 100 ml.) is treated with 1 drop to 2 ml. (according to the presumed concentration of the β-naphthol) of $N/10$ sodium nitrite solution (0·69 g. in 100 ml.) and a volume of N hydrochloric acid equal to that of the nitrite solution, and the volume of the liquid is made up to 10 ml. with water, there develops a pink to red colour. The time required for the formation of the colour decreases from a few minutes to a few seconds with increasing quantities of the naphthol, and at the same time the stability of the colour decreases from several hours to about 15 minutes. The sensitivity of the reaction can be increased still further by diluting to less than 10 ml.

A drop reaction can be carried out by mixing on a porcelain plate 1 drop of the β-naphthol solution, 1 drop of the nitrite solution, and 1 drop of the acid. Under these conditions an $M/10{,}000$ β-naphthol solution gives a pink colour in about 10 minutes.

Colorimetric Determination.—A scale of colours is formed by diluting to 10 ml.

volumes of the naphthol solution ranging from 0·10 to 5 ml. and treating the solution with volumes of the nitrite solution and acid equal to half the volume of the naphthol solution (with a minimum of 2 drops of the acid). The colour of the test solution may be compared with these standards by dilution or in a colorimeter. Because of the difficulty of comparing deep red colours in the colorimeter it is of advantage to use a continuous scale of colours including that of the supposed concentration of the naphthol solution. The standard colours should be prepared at the same time as that of the solution under test. E. M. P.

Analysis of Natural Perfumes by Entrainment at Low Pressure with Ethylene Glycol. S. Sabetay. (*Ann. Chim. anal.*, 1939, **21**, 173–176.)—Simple and rapid methods for the analysis of natural perfumes are dependent on a distillation process, and distillation in superheated steam has been found satisfactory for control work by Naves, Sabetay and Palfray (*id.*, 1937, **19**, 201). A simpler method is based on the fact (use of which is made in industrial operations) that in a vacuum the volatile fractions of most natural perfumes are entrained by the vapour of ethylene glycol. From 1 to 10 g. of the sample are treated in a 50 to 75-ml. Vigreux vacuum distillation-flask with 20 ml. of ethylene glycol, and distillation is carried out at 8 to 15 mm. pressure and 90° to 100° C. in an oil-bath, which is maintained at 125° to 145° C. The residue is then usually odourless, but as a precaution a second distillation is carried out with a further 20 ml. of ethylene glycol, the distillate being collected separately. Exceptionally a third similar distillation may be necessary, and an indication of whether it is required is obtained on adding 100 and 50 ml. of water to the first and second distillates, respectively; if no appreciable quantity of oil separates from the latter, the third distillation is unnecessary. The diluted distillates are then saturated with salt (about 30 g.) and extracted in succession with three 20-ml. portions of a mixture in equal volumes of pentane and ether; this mixture dissolves only negligible quantities of the ethylene glycol, and for this reason is preferable to ether alone. A fourth or fifth extraction may be required in exceptional cases. The solvent mixture is dried by means of anhydrous sodium sulphate and filtered, and the filter is washed with some of the solvent. The filtrate is then evaporated in a tared flask at 15 to 20 mm. pressure, until there is no further loss in weight, and the weighed residue, which consists of the true perfume, is subjected to olfactory examination, and its physico-chemical constants are determined. The method gives results which agree satisfactorily with those obtained by the method of Naves, Sabetay and Palfray (*loc. cit.*). Since ethyl phthalate is also carried over to a great extent by the ethylene glycol, tests for the former in the distillate (*cf.* Naves and Sabetay, ANALYST, 1938, **63**, 208) will reveal adulteration of this nature. Below are summarised (*a*) the yields (percentages), (*b*) the n_D^{20} of the volatile fractions separated from a number of perfumes in this way, and (*c*) the number of distillations necessary, respectively:—Jasmine, (*a*) 15, (*b*) 1·5001, (*c*) 1; jasmine (absolute), (*a*) 30·70, (*b*) 1·4963, (*c*) 2; rose, (*a*) 30·50, (*b*) 1·5055, (*c*) 1; rose (absolute), (*a*) 51·1, (*b*) 1·5116, (*c*) 1; orange (absolute), (*a*) 42, (*b*) 1·4883, (*c*) 1; violet (absolute), (*a*) 7·10 (nonadienal, 42·8 per cent.), (*b*) 1·4834, (*c*) 1; polyanthus (absolute), (*a*) 14·5, (*b*) 1·5319, (*c*) 1; lavender (absolute), (*a*) 73·6, (*b*) 1·4690, (*c*) 1; ***Boronia megastigma***, (*a*) 19·4 (β-ionone, 41·5 per cent.), (*b*) 1·4786, (*c*) 2; immortelle, (*a*) 4·9, (*b*) 1·5032, (*c*) 2; geranium (absolute), (*a*) 84·2, (*b*) 1·4771, (*c*) 1; musk, (*a*) 7·6, (*b*) 1·4923, (*c*) 1; Mousse de Chêne, (*a*) 7·3, —, (*c*) 2; civet, (*a*) 9·3, —, (*c*) 2. J. G.

Improved Method for the Determination of the Acidity and *p*H of Paper. H. F. Launer. (*J. Res. Nat. Bur. Stand.*, 1939, **22**, 553–564; *Chemical Age*, 1939, **41**, 25.)—At present it is usual to prepare an extract of paper for determinations of *p*H and acidity by extracting 5 g. with 250 ml. of distilled water under a reflux condenser for 1 hour in a water-bath at 95° to 100° C. (but not boiling). This method has been criticised (*cf.* Grant, *Proc. Tech. Sect. Paper Makers' Assoc.*, 1939, **19**; in the press), and the author has now found that the *p*H values of such extracts are very susceptible to variations in the duration and temperature of the extraction, and that the same *p*H values are obtained by the following method, which, however, is less affected by such influences:—The paper (1 g., air-dry) is macerated with 20 ml. of distilled water until wet, 50 ml. of water are added, and the mixture is allowed to stand at 20° to 30° C. for at least 30 minutes (preferably for 1 hour). The *p*H of the extract can then be determined without removing the paper, thus avoiding errors due to filtration and to incidental contamination by the atmosphere inherent in the present method. Thick kraft papers should first be ground, presumably in a mill of the Koerner type (see Burton and Rasch, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 605), which is used at present and which enables the paper to be disintegrated without contamination or overheating; with such papers the period of extraction should be 20 hours. The standard procedure specified by the A.S.T.M. for the purification of the water used is considered unnecessarily severe, as the *p*H of the water need not be exactly 7, the same results being obtained with waters of *p*H 6·7 and 5·9. The *p*H values obtained by the method now described correspond satisfactorily with the amounts of alum used, and are equivalent to hydrogen ion concentrations of about 25 per cent. of those obtained by the standard method. J. G.

Examination of Writing made with Aniline Dyes. F. Künkele. (*Z. Unters. Lebensm.*, 1939, **77**, 596–602.)—In the chemical and physical examination of ink marks much less depends upon the identification of the dye than upon clearly establishing distinct differences between one mark and another. Similarities are of value only when the ink contains unusual constituents. In a preliminary examination with the naked eye differences are often apparent, but small differences in colour should be interpreted with caution, since they are often due to differences in the rate of movement of the pen, and still more often to the age of the document, the cleanliness of the ink, the kind of paper and the preservative constituent of the ink. On the other hand, especially with the rarer dyes, colours similar in appearance may be chemically different. The microscopical examination of marks made with aniline inks rarely gives useful results unless one of the inks contained deposits caused by dirt, dust or admixture with other ink. Many inks give a characteristic fluorescence in ultra-violet light. The test is useful, but mere colour differences which are not recognisable as distinct fluorescence should be disregarded. Occasionally, more definite results are obtained if the mark is first moistened with water and alcohol and dried. The reagents recommended for the examination of modern aniline inks are water, alcohol (96 per cent.), conc. sulphuric acid and 10 per cent. solutions of hydrochloric acid, ammonia and potassium hydroxide. A mark is lightly rubbed with a small cotton-wool pad charged with alcohol which dissolves the dye and gives a true indication of its colour. Another mark is treated with a drop of conc. sulphuric acid, which gives an immediate reaction with many dyes. After 30 seconds two drops of water are added and mixing is effected by blowing through a capillary tube (9 to 10 cm. long and 1 mm. internal diameter) held 1 to 2 cm. above the surface of the drop. In many instances a distinct colour change follows the addition of water. Other marks are treated with drops of 10 per cent. hydrochloric acid, 10 per cent. ammonia and 10 per cent. potassium hydroxide solutions. The last two reagents do not give characteristic reactions with many dyes. The reactions should be observed within 30 seconds, after which the drops are drawn up on filter-paper and, if necessary for the safety of the document, the places treated may be neutralised with ammonia or dilute acetic acid. It is often advisable to place a drop of water on the mark and transfer the solution of the dye by means of a capillary tube to a porcelain plate on which the drop is allowed to dry before being subjected to the tests. When the document has no special value, the stained fibres may be removed by gentle scraping and examined through binocular lenses in an appropriate light. Black inks, which are often mixtures of dyes, are not easily differentiated. The following procedure is frequently applicable. A strongly tinted mark is moistened with a little water and lightly rubbed, and the solution is transferred to a porcelain plate and concentrated by gentle evaporation. The surface of the drop is touched uniformly with the end of a strip of filter-paper, 1 mm. broad, held vertically. Red and green dyes rise more rapidly and to greater heights than the blue constituents, so that a separation is effected. Individual blue ink markings are often differentiated by exact observation of the chemical tests, especially those with hydrochloric acid and ammonia and particularly with marks of equal colour intensity on the same document. In many instances Feigl's method of distinguishing acidic and basic dyes (*Qualitative Analyse mit Hilfe der Tüpfelreaktionen*, Leipzig, 1938, p. 498) is useful. Sufficient stearic acid and urea to form layers 0·5 cm. deep are melted in a test-tube. Cuttings or scrapings from the document are placed in the mixture, which is then warmed for a short time. Acidic dyes colour the lower urea layer and basic dyes the upper stearic acid layer. Modern iron-gall inks contain an aniline dye which provides the colour before the latent iron tannate colour forms on the paper. When treated with a drop of water the aniline dye usually dissolves before the iron tannate, especially if the document is old, and the dye may thus be separated for testing. An exhaustive list of the aniline dyes used in ink manufacture cannot be given. According to Becher (*Die Fabrikation der Tinten, Tuschen und Stempelfarben*, Augsburg, 1936), the following are some of the dyes commonly used:—Acidic dyes: nigrosin, Agalma-black TG, brilliant black BX, naphthylamine black S, naphthol blue-black, "artificial silk black" 3G, Neptune blue R, cyanol extra, water blue I, alkali blue 7, light green SF, green PLX, Neptune green SGO and SBX, alkali fast green 3G, Havanna brown G, Neptune brown RX, eosin A salt-free T, acid fuchsin O, brilliant crocein MOOL, ponceau RR, sorbic red X, orange II, orange GG, tartrazin XX, fast yellow Y, quinoline yellow KT, metanil yellow extra. Basic dyes: methylene blue, marine blue, Victoria blue B, Victoria pure blue BO, methyl violet, crystal violet, ethyl violet, diamond green BXX (malachite green), fuchsin A, rhodamine B extra, safranine T, chrysoidine RL, euchrysine.

A. O. J.

Inorganic

Determination of Zinc and Copper with Morpholine. L. S. Malowan. (*Mikrochem.*, 1939, **26**, 319–321.)—Morpholine (O:$(CH_2CH_2)_2$:NH), a cyclic amine which is miscible with water in all proportions, yields precipitates, insoluble in excess of the reagent, with a number of metals, including zinc and copper, which form soluble complex salts with excess of ammonia. The precipitates are crystalline and easy to filter. The reagent may be used for the determination of zinc and of copper from pure solutions, with results as accurate as those obtained by the sodium carbonate and potassium hydroxide methods. J. W. M.

Group Separation of the Rare Earths by means of Sulphamic Acid. J. Kleinberg, W. A. Taebel and L. F. Audrieth. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 368–369.)—The grouping of the rare earths by means of sodium sulphate into lanthana and yttria earths may be efficiently accomplished by conversion of the earths into sulphamates, and gradual treatment of the ice-cold solution with solid sodium nitrite until the neodymium absorption line 637$m\mu$ disappears.

W. R. S.

Simultaneous Determination of Zirconium and Hafnium by means of Selenious Acid. A. Claassen. (*Z. anal. Chem.*, 1939, **117**, 252–261.)—The author has investigated the precipitation of zirconium as basic selenite (Simpson and Schumb, ANALYST, 1931, **56**, 337), and succeeded in converting it into the normal selenite $Zr(SeO_3)_2$, which is crystalline and of stoichiometrically definite composition. This was determined gravimetrically by ignition (1000° C.) of the precipitate previously dried at 120° to 200° C., and volumetrically by iodimetric determination of the selenious acid after solution of the precipitate in sulphuric acid and sodium fluoride. Hafnium behaves like zirconium, yielding a basic selenite convertible into the normal compound. The gravimetric determination of hafnium in the selenite gives a mean positive error of 1 per cent., the volumetric determination an error of 1·4 per cent. The indirect simultaneous determination of the two elements in the mixed selenite precipitate is carried out as follows:—

The slightly acid solution (maximum, 0·6 *N* sulphuric or hydrochloric acid, but 0·3 *N* for small quantities of zirconium; maximum for nitric acid 0·38 *N*; volume, 400 ml. for 0·1 g. of zirconium) is precipitated in the cold with 2 g. of selenious acid in 10 per cent. solution, heated to boiling, and set aside for 5 to 20 hours on a steam-bath or hot plate until the flocculent precipitate has become dense and crystalline. It is collected in a Jena filtration crucible (G4) for the gravimetric determination or on a paper filter for the volumetric determination, washed eight times by decantation with hot water (hot dilute hydrochloric acid may be used if other elements are present), then with cold water until the washings give no selenium reaction with starch, potassium iodide and dilute sulphuric acid. For the gravimetric determination, the crucible and its contents are dried at 120° to 200° C. and ignited to constant weight; 0·1000 g. of ZrO_2 yields 0·2801 g. of $Zr(SeO_3)_2$; 0·1000 g. of HfO_2 yields 0·2054 g. of $Hf(SeO_3)_2$.

The volumetric determination is preferable on account of the greater difference between the two conversion factors: 0·1000 g. of ZrO_2 as selenite consumes 64·92 ml. of 0·1 *N* thiosulphate solution; 0·1000 g. of HfO_2 consumes 37·99 ml. The mixed selenite precipitate is rinsed off the filter with a little water and dissolved by gentle heating with 6 ml. of sulphuric acid (1:1) and 10 ml. of 3 per cent. sodium fluoride solution, the warm solution is filtered through the same paper into a 750-ml. conical flask, and the paper is washed with a little dilute acid containing fluoride. The cold solution is diluted (200 to 300 ml.), treated with 10 to 15 ml. of 2 per cent. starch solution, a little sodium bicarbonate and a solution of 4 g. of potassium iodide free from iodate, and titrated after 2 minutes with 0·1 *N* thiosulphate solution. The excess of starch is added for the purpose of keeping the selenium in colloidal solution, thus preventing it from adsorbing iodine. As the titration proceeds, the dark blue solution becomes lighter, then dirty brown; the end-point, a sudden change to pale red, is accurate to one drop, especially if the flask rests on an illuminated pane of opal glass. The volumetric determination gives results reproducible within 0·3 per cent.; the hafnium content in zirconium can be determined within 1 per cent., if an empirical hafnium factor (*i.e.* the theoretical factor multiplied by 1·01) for the thiosulphate solution is used. W. R. S.

Colorimetric Determination of Fluorine with Ferron. J. J. Fahey. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 362–363.)—The reagent is made up from two solutions: (i) a 0·1 *N* solution of ferric chloride in 0·2 *N* hydrochloric acid, and (ii) a saturated aqueous solution of ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid). Ten ml. of (i) are mixed with 90 ml. of (ii), and 100 ml. of water. The reagent is quite stable. For the determination of fluorine in rocks, 0·5 g. is fused with 5 g. of sodium carbonate in a platinum crucible until the mass is fluid. The melt is leached overnight with 300 ml. of water in a platinum dish, the extract is heated just to boiling, the residue is washed once with water, returned and boiled for a minute with 100 ml. of water, the liquid is again filtered, and the residue is washed with hot water. The filtrate is treated in a platinum dish with a solution of 1 g. of zinc oxide in 30 ml. of hydrochloric acid (1:3), and boiled, and the precipitate is allowed to settle, collected, and washed in the same way as the preceding precipitate. The filtrate is accurately divided into two parts. One of these is neutralised to methyl orange with hydrochloric acid (1:19); the other is treated with exactly the same amount of acid without the indicator, a solution of 0·5 g. of zinc oxide and 1 g. of ammonium carbonate in 2 ml. of strong ammonia and 10 ml. of water, and gently boiled until no odour of ammonia can be detected, the volume being reduced to about 75 ml. The solution is diluted with 50 ml. of water, stirred and filtered, and the precipitate is washed as described above. The filtrate is made up to 250 ml., a concentration of 0·1 to 1·5 mg. of fluorine in 25 ml. being aimed at; if the rock contains less than 0·2 per cent. of fluorine, 1 g. should be taken, and the final filtrate concentrated to 50 ml.

A 25-ml. portion contained in a 50-ml. beaker, and a standard of the same pH and sodium chloride concentration, are treated with 2·00 ml. of reagent and placed in a colorimeter, and the standard is treated with a 0·02 *N* solution of sodium fluoride until its relatively green tint matches the yellow green of the unknown solution, the latter being suitably diluted so that equal volumes are maintained in the two vessels. A difference in tints is apparent with as little as 0·05 mg. of fluorine. With natural waters containing less than 1000 parts of total solids per million, the sensitiveness is twice as great, allowing 0·025 mg. to be determined in a 25-ml. portion. The method may be used with minerals containing up to 10 per cent. of fluorine; beyond this percentage, the error incurred in the colorimetric determination is too great for accurate work. W. R. S.

Microchemical

Examination of Pigments in Painting. E. Bontinck. (*Mikrochem.*, 1939, **26**, 182–188.)—Various tests are examined for the detection of sulphur in lapis lazuli, ultramarine and other mineral pigments which contain sulphur. Feigl's iodine-azide test may give erroneous positive results owing to the presence of sulphur in the oil medium. It is recommended to treat the pigment with 6 *N*-acetic acid on a small silver plate. The resultant black spot of silver sulphide is clearly visible even with a particle 0·005 mm. in diameter. A reaction to distinguish between lapis lazuli and ultramarine is unnecessary, as they are quite distinctive under the microscope. Contrary to what has previously been stated, lapis lazuli is decolorised by dilute acetic acid (by 0·02 *N* acetic acid after 24 hours, but not by 0·01 *N* acetic acid). J. W. M.

Colorimetric Micro-determination of some Phenols. A. I. Matiu, C. Popesco and A. Popesco. (*J. Pharm. Chim.*, 1939, **30**, 49–58.)—The basis of the method, as applied to the determination of phenols, is the formation of a blue colour with a phosphotungstic reagent, followed by the discharge of the colour by titration with potassium ferricyanide solution. The method can be used for the determination of pyrocatechol, hydroquinone, pyrogallol, gallic acid and tannins, but is not applicable to those phenols the reducing power of which is too low for the blue colour to be formed with the phosphotungstic reagent.

Reagents.—(1) *Phosphotungstic reagent*: Ten g. of sodium tungstate, 8 ml. of phosphoric acid (sp.gr. 1·71) and 90 ml. of water are boiled together for 1½ hours beneath a reflux condenser. After cooling, the volume is made up to 100 ml. (2) *Solution of sodium carbonate* (*crystalline*): A 20 per cent. solution. (3) *N*/10 *Ferricyanide solution*: Potassium ferricyanide (1·65 g.) and potassium hydroxide (1·65 g.) are dissolved in 100 ml. of water, and the solution is standardised by Mohr's method (Barral, *Précis d'Analyse Chimique Quantitative*, Paris, 1927, p. 490). (4) *Phenol solution*: About 1 g. in 1000 ml.

Procedure.—A measured volume of the phenol solution is treated with the phosphotungstic reagent and the mixture is made alkaline with the sodium carbonate solution, when there develops a blue colour the depth of which is proportional to the quantity of phenol present. The ferricyanide solution is added from a micro-burette until the colour is discharged. The following table shows the volumes of phenol solution, phosphotungstic reagent and sodium carbonate solution used, the colour of the liquid at the end-point, and the weight of phenol (in g.) equivalent to 1 ml. of $N/10$ potassium ferricyanide solution.

	Phenol solution ml.	Phospho-tungstic reagent ml.	Sodium carbonate solution ml.	Colour of final liquid	1 ml. of ferri-cyanide solution equivalent to phenol g.
Pyrocatechol					
	0·5	2	30	Pink	0·001376
	1·0	4	30		
	1·5	6	30		
	2·0	8	30		
Hydroquinone					
	0·5	2	30	Pale yellow	0·002752
	1·0	4	30		
	1·5	6	30		
	2·0	8	30		
Pyrogallol					
	0·5	4	20	Yellow	0·001051
	1·0	4	20		
	1·5	4	20		
Gallic acid					
	0·5	4	20		0·001567
	1·0	4	20		
	1·5	4	20		
Tannin					
	0·5	2	[illegible]		0·001923
	1·0	2	20		
	1·5	2	20		
	2·0	2	[illegible]		
Tannigene					
	0·5	2	[illegible]		0·002525
	1·0	2	20		
	1·5	2	20		
	2·0	2	[illegible]		
Tannoforme					
	0·5	2	[illegible]		0·002058
	1·0	2	20		
	1·5	2	20		
	2·0	2	[illegible]		
Quinine tannate					
	0·5	2	[illegible]		0·003125
	1·0	2	20		
	1·5	2	20		
	2·0	2	[illegible]		

In the analysis of tannin-containing medicinal products such as Tannigene, Tannoforme, and quinine tannate, the product is dissolved, and the tannin is liberated by treatment with sodium hydroxide for the first two and hydrochloric acid for the quinine tannate. E. M. P.

Colorimetric Micro-method for the Estimation of Nitrates. Pesez. (*J. Pharm. Chim.*, 1939, **30**, 112–117.)—In presence of sulphuric acid, nitrates convert nitrobenzene into dinitrobenzene, and the latter condenses with acetone in alkaline solution to give a violet-red colour, the intensity of which is proportional to the amount of nitrate originally taken. Quite small amounts of nitrate can be estimated in this way, the procedure being as follows:—One to 10 ml. of the solution to be tested, depending on the amount of nitrate present, is measured into a porcelain dish and evaporated to dryness after being neutralised by the addition of two drops of ammonia. A drop of nitrobenzene is added to the residue, and then 15 drops of conc. sulphuric acid, care being taken that these fall on to the nitrobenzene and not on to the dry residue of nitrate. The liquid is stirred with a small glass rod for 2 or 3 minutes and is then treated with 5 ml. of acetone; the mixture, after further stirring, is transferred to a stoppered tube, with the aid of a further 5 ml. of acetone. Five ml. of 15 per cent. sodium hydroxide solution are added, and the tube is tightly stoppered, shaken, and allowed to stand for 10 minutes, after which the colour of the solution is compared in a colorimeter with that of a solution prepared in the same way from a known amount of nitrate.

The reaction is sufficiently sensitive to be used for the estimation of nitrate in water, but chlorides must first be removed. Nitrites, however, do not interfere. To 20 ml. of the suspected water are added 2 drops of 20 per cent. sulphuric acid and then a 0·05 *N* solution of silver sulphate, drop by drop, until a drop of the liquid just gives a brown colour with potassium chromate paper. The liquid is then filtered, and exactly half the filtrate, equivalent to 10 ml. of the water, is evaporated to dryness after being neutralised with 2 drops of ammonia. The remainder of the estimation is carried out as described above. Quantities of potassium nitrate ranging from 25 to 50 mg. per litre were estimated with an error of about 10 per cent., even in presence of 200 mg. of sodium chloride per litre.

F. A. R.

Determination of Potassium with Magnesium Dipicrylamine. R. Dworzak and H. Ballezo. (*Mikrochem.*, 1939, **26**, 322–342.)—The method has been adapted to the determination of potassium in mineral waters. It gives satisfactory results in presence of up to 100 times the amount of sodium when excess of wash-liquid, saturated with the potassium salt, is used. The reagent solution (which is also used for washing purposes) is prepared from 19·6 ml. of an approximately 0·25 *N* solution of pure magnesium dipicrylamine, to which is added 2 ml. of a potassium chloride solution containing 1 mg. per ml.; the mixture is left for 4 hours and diluted with 50 ml. of water, and may be used the following day. The reagent is filtered immediately before use. A porcelain crucible is used for the precipitation: a porcelain filter-stick for the filtration. It is advisable to use a 50 per cent. excess of reagent. The precipitate should be cooled for 7 hours and then left for 3 days before filtering. It is then washed with the reagent solution and finally with ether and dried at 85° to 95° C. J. W. M.

Microchemical Reactions for Scandium. G. Beck. (*Mikrochim. Acta*, 1937, 2, 9–12). The following reagents are particularly suitable for tests for scandium in minerals:—morine, which gives a green fluorescence extinguished by alkali fluorides; alizarine sodium sulphonate in slightly acid solutions, which gives a precipitate; aurine tricarboxylic acid, which gives a red precipitate soluble in ammonia to form a yellow-brown solution (the precipitate formed by aluminium is not soluble in ammonia). Luteo cobalt nitrate gives a yellow-brown crystalline precipitate of $[Co_2(NH_3)_6][ScF_6]$ with complex solutions of scandium fluoride. This reagent also reacts with aluminium, beryllium and zirconium in acid solution to form amorphous precipitates; in ammonium carbonate solution, beryllium does not react, and zirconium gives an amorphous precipitate. The crystals of the aluminium and scandium compounds are readily distinguished. Magnesium in ammoniacal solution forms an easily recognisable crystalline product with the cobalt reagent. J. W. M.

Reviews

THE PHASE RULE AND ITS APPLICATIONS. By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C., revised with the assistance of A. N. CAMPBELL, D.Sc., F.I.C. Eighth Edition. Pp. xv + 327, with 163 figures. London: Longmans, Green & Co. Ltd. 1938. Price 12s. 6d. net.

As a guide and means of classification in the study of chemical equilibria in systems other than those which are wholly gaseous, the Phase Rule is still of particular value. Professor Findlay's exposition, first published in 1904 and long regarded as the standard English text-book on the Phase Rule, has been brought up to date again (editions were reviewed in THE ANALYST, 1923, 575; 1928, 244), and work published as late as 1938 is included. References to applications of X-ray analysis in Phase Rule problems are welcome additions, but it is to be hoped that in the next edition a more even balance will be struck between the applications to "non-metallic" systems and "metallic" systems, as the latter seem somewhat neglected in view of the present importance of alloys.

There are a few slips, such as a reference (p. 34) to the Appendix dealing with the experimental determination of the transition point, which has been omitted from the present edition, and it is a little confusing to speak of heated mercury *subliming* through a layer of liquid bromonaphthalene (p. 92), in view of the implied definition of sublimation (p. 21). However, the analyst will find underlying principles to guide him in some of his problems, as in converting insoluble systems into soluble systems by fusion (p. 287), and a word of warning that different substances with identical melting-points do not necessarily depress each others' melting-points on admixture (p. 124).

Notwithstanding such minor criticisms, this edition is a worthy successor to its predecessors. J. G. A. GRIFFITHS

MAY'S CHEMISTRY OF SYNTHETIC DRUGS. By PERCY MAY, D.Sc. (Lond.), F.I.C., and G. MALCOLM DYSON, Ph.D., F.I.C., A.M.I.Chem.E. 4th Edition. Pp. xii + 370. London: Longmans, Green & Co. Ltd. Price 21s.

Of the nature of drug action very little is known with certainty, but theories have been advanced from time to time, such as those of Ehrlich, who makes an analogy with dye action, and of Loew, who correlates physiological activity with the chemical affinity of a drug for aldehyde and amino groups, and the more modern theory of biochemical interference, which postulates modification of enzyme activity as the controlling factor. On the other hand, the manner in which a drug reaches the seat of its action is better understood, being in a measure dependent on physical properties, particularly solubility. Overton and Meyer, for example, long ago showed that a close relationship exists between the effectiveness of narcotics and their distribution coefficients between lipoid substances and water. It is with such ideas that the authors of this book are concerned in the three introductory chapters, which summarise the principles by which the chemist is guided when synthesising a new drug.

Chapter II is devoted to the physiological effects which are frequently associated with different atoms and groups, as for example, the action, on the central nervous system, of ethyl groups when introduced into a suitable molecule. A list of generalisations, known as Schmiedeberg's Rules, is followed by a discussion of the more important atoms and groups from this point of view, including the effect of unsaturation and stereoisomerism.

The subject of the next section—the chemical changes which drugs undergo in the organism—is of considerable importance, since a study of the elimination products of a drug may give a clue to its mode of action and even indicate the manner in which its structure can be modified in order to decrease its toxicity. As is mentioned later in the book, the discovery that aniline and its simple derivatives are eliminated from the body as a compound of *p*-aminophenol and glycuronic acid led eventually to the synthesis of phenacetin.

Following this general treatment is the main subject matter of the book which, owing to its diversity, offers some difficulty of presentation. The authors have not attempted a hard and fast systematic treatment throughout, but have chosen for their chapter headings the strongest common relationships between the substances described therein. Thus sometimes similar physiological effect is the keynote, as, for example, "Narcotics and General Anaesthetics," and at other times common chemical origin ("Adrenaline and other Derivatives of Ethylamine"). In fairness it must be said that this method produces a good sequence within the chapters, and possibly a more rigid classification would have produced a less readable book.

Since several of the natural alkaloids and many "artificial" ones have now been synthesised, this branch of the subject receives a considerable share of treatment. After an introductory chapter dealing with active groupings in alkaloidal structure, there follows an account of quinine and its derivatives, the alkyl hydro cupreines, and various quinine compounds of therapeutic value. Substitutes for quinine, such as Plasmoquin, are also described. Next we have the properties and syntheses of atropine and the tropeines, followed by cocaine and its substitutes, the eucaines, stovaine, novocaine and other local anaesthetics. Although morphine itself has never been synthesised, many attempts have been made to prepare derivatives of it and to produce compounds containing similar groupings. In view of this, a résumé is given of the chemistry of morphine and its related alkaloids including members of the apomorphine group. Narcotine, papaverine, hydrastine and others of the isoquinoline group receive similar treatment and, wherever possible, full syntheses are indicated with references to the original work.

Because of the powerful physiological effect of many derivatives of ethylamine, these compounds have been grouped together under one heading and include adrenaline, ephedrine, benzedrine, histamine and similar bodies.

The most notable expansion of this edition is due to the addition of a chapter on Hormones and Vitamins. To condense such a subject into twenty pages was a bold undertaking, but the authors have at least succeeded in producing a useful summary of some of the results achieved. Syntheses of vitamins A, B_1, B_2 and C are given, and mention is made of the recent success in producing α-tocopherol (vitamin E). The hormones are represented by thyroxin and the sex hormones. It is obviously impossible to give more than a brief outline of the latter in such limited space, and the treatment has been confined to their origin, mode of action and relationships one to another. A useful diagram showing the mechanism of the action of the female sex hormones is given, and mention is made of the recently discovered synthetic derivatives of stilbene, whose activity actually exceeds that of oestrone. A list of references would have been a useful addition here for the reader who may require further information.

Organic antiseptics include the therapeutically active dyes (triphenylmethane series, trypan blue, etc.), the complex ureas (Bayer 205, S.U.P.), the sulphonamides and acridine derivatives (acriflavine, atebrin).

Compounds containing metals in combination are treated in two sections—the first dealing with those of mercury, silver and gold, and the second with those of arsenic, antimony and bismuth. These include most of the well-known general antiseptics and anti-syphilitics and need not be further commented upon here.

It is impossible in a review of this length to touch upon everything in the book; let it suffice to say that the authors have omitted very little of their legitimate subject matter. A justified criticism would appear to be that they have at times gone outside the scope of the title.

The book will be of considerable use to the organic chemist interested in the synthesis of drugs, and a source of stimulating ideas to all chemists, on account of the many ingenious synthetic methods abstracted from the freely-quoted patent literature. It will also be of considerable use as a reference book in view of the comprehensive index that it possesses. Finally, the account of many beautiful syntheses, invariably represented by graphic formulae, will be a useful aid to the student and save him much weary searching of the textbooks.

G. E. H. SKRIMSHIRE

Casein and its Industrial Applications. By **Edwin Sutermeister**, S.B., and **Frederick L. Browne**, Ph.D. Second Edition. Pp. 433, with 35 Tables and 50 Figures. New York: The Rheinhold Publishing Corporation; London: Chapman & Hall, Ltd. 1939. Price 32s. 6d. net.

A new edition of Sutermeister is something of a major event in the casein world. The first edition appeared in 1927, when the industry was, relatively speaking, in its infancy, and at that time the book was more than a mere review of current practice and literature. It carried out invaluable pioneer work in pointing out the possibilities of the industry and emphasising the need for scientific control. In 1927, as now, the book impressed by virtue of its reasoned judgment. It has helped the development of casein by countering the somewhat extravagant claims made from time to time.

Even if in some degree the casein industry has not fulfilled the promise of its youth, it has developed to an extent which has made sections of the early Sutermeister begin to date. Eight of the original eleven contributors have collaborated in the new edition and parts of the book have been completely rewritten. Parts are new not only in matter but also in emphasis. For example, in the United States the whole attitude towards casein manufacture has changed. When the first edition of the book appeared, casein was largely a by-product of the creameries, made in the simplest and cheapest plant available, with little control or scientific method. It is not surprising that the variable nature of casein made under such conditions led to a prejudice in favour of competitive materials and placed the industry under a handicap still felt to-day. Now casein of uniformly high quality is so widely available that material made by the old "hit or miss" methods is difficult to sell. Sutermeister can claim much of the credit for this improvement by the emphasis laid on scientific control in 1927.

Naturally the book has a strong American colouring, and statistics are mostly confined to the States. This colouring may be misleading, for some of the statements are not applicable to the British Empire. At any rate in the States, the vat method of self-souring would appear to have receded in importance in favour of "continuous" processes, and the latter, mentioned more or less in passing in the earlier edition, now receive detailed description. One "continuous" process, the Sheffield method of hydrochloric acid precipitation, is described at considerable length and would appear to be perhaps the chief development in manufacturing technique since 1927.

Although the book has been considerably enlarged, its fundamental honesty becomes apparent as much by its omissions as its additions. On carefully comparing sections, the disappearance of many minor applications of casein, which were pious hopes in 1927, but failed to become established on any appreciable scale, is noteworthy.

According to statistics quoted, the manufacture of casein in the States in 1937 was about five to eight times what it was in the immediate post-War years, and the consumption about three times. By far the greater part of this, possibly over 70 per cent., was used in paper coating. Plastics claim over 10 per cent. as second on the list, and the major usage in this field is in the manufacture of buttons. The chapter on paper-making contains little of novelty, and here the improvement in the quality and reliability of casein has been the largest factor in its extended use. The chapter on plastics admirably reflects the changes of the last ten years, and the increase of the bibliography from 66 references in 1927 to over 400 in the new edition tells its own story. Even if the employment of casein in the manufacture of buttons stands out most prominently, other applications are still more than mere optimism, and the battle with phenol resins has not gone entirely one way.

The fascinating new development of "Lanital," synthetic textile fibres from casein, is fully described and, although the future of this product cannot yet be predicted, it would appear to have wide possibilities and is already being made on a fairly large scale in Italy.

The section on glues has been carefully revised and some valuable observations on "working life" added. Casein paints have developed markedly since the earlier edition of the book, and paste paints are virtually an innovation which has become firmly established since 1927. The chapter on paints has also been enlarged, and the bibliography both on glues and on paints considerably extended.

The chapter on the testing and analysis of casein has been brought up to date, and has been placed in a more prominent position in the book instead of being relegated to the end. The notes on ash determination are of special interest, even if the relationship between proximate ash-content and viscosity may be open to doubt.

Lastly, it remains to congratulate the authors and the publishers on the improved appearance of the book, the excellent quality of the illustrations and the increased clarity of the diagrams and tables. It is not unreasonable to assume that improvements in the quality of casein have played a part in this!

E. W. PATES

ORGANIC CHEMISTRY. Professor PAUL KARRER. Translated from the latest German edition by A. J. MEE. Pp. xx + 902. Elsevier Publishing Co., Ltd., Amsterdam and London. 1938. Price 45s.

In the preface the author states that his aim was to provide students with a textbook of organic chemistry of medium size which would give them a survey of the ever-increasing body of facts, and it may be said at once that he has succeeded in an admirable and praiseworthy manner.

In dealing with the main body of the subject, the historical and usual division into aliphatic, carbocyclic and heterocyclic compounds has been retained, although not slavishly followed. In each section the compounds are regarded as derivatives of the hydrocarbons and have been arranged, as far as possible, according to their functional groups.

As might be anticipated from a survey of the investigations in which Professor Karrer has played so brilliant a part, considerable prominence is given to the chemistry of naturally occurring substances, and various biochemical topics are dealt with in some detail. As some of the most striking and fruitful developments in the whole of organic chemistry in recent years have lain in the borderland of chemistry and biology, this emphasis on the biological aspect enhances in a very real way the value and utility of this book to the present-day student.

Although the number and variety of compounds dealt with are both large and extensive, the book is eminently readable; it is far from being of the dictionary type and deals with synthetical methods in considerable detail.

By way of criticism it may be pointed out that the application of the principles of the electronic theory of valency receives scant and cursory treatment and is not even mentioned in the detailed index; it is surprising also to find numerous structural formulae in which nitrogen is represented as a penta-covalent element and many in which sulphur functions as a hexa-covalent element. The physico-chemical side of the subject is referred to here and there in an incidental and almost casual manner.

Whilst these omissions, from a textbook intended for the general student, of some of the more important developments on the theoretical side result in a certain loss of balance in the presentation of the subject, they do not seriously impair the general excellence of the work.

English students suffer from no lack of valuable monographs dealing with the theoretical and physico-chemical aspects of organic reactions, and they should be grateful that Professor Karrer has emphasised those sections of chemistry to which the term organic was originally applied.

The volume concludes with numerous tables of data which are both useful and interesting.

The translation has been well done and the English version reads smoothly and easily. The publishers have done their part well in the general make-up of the book; the paper is opaque, the type clear and legible and the binding strong and substantial.

It is to be regretted that the high cost may hinder the wide circulation that the book deserves and ought to have. J. KENYON

ANLEITUNG ZUR ORGANISCHEN QUALITATIVEN ANALYSE. By H. STAUDINGER and W. KERN. 3rd Edition. Pp. xvi + 157. Berlin: Julius Springer. 1939. Price RM.6.90.

This well-known textbook has undergone little essential change since the previous edition of 1929. It has, however, been revised and brought up to date by the inclusion of much new material. Thus one finds descriptions of the use of Girard's reagent for aldehydes and ketones, dinitrochlorobenzene for phenols, anthraquinone-β-carboxylic acid for alcohols, di-*p*-dimethylaminophenyl-carbodiimide for acids, and other reagents of a similar nature.

This is not a textbook that can be used by itself for the complete identification of individual substances. It is a guide or key (Anleitung) to assist the student in classifying an unknown compound, so that, having put it into the right pigeon-hole, he will be able to identify it more easily. For this final stage, the student is referred to Kempf and Kutter's *Schmelzpunktstabellen zur organischen Molecularanalyse.* Dr. Staudinger's system of classification consists in dividing substances first into two groups, namely, those that boil below 160° C. and those that boil above that temperature, and then each group into five sub-groups according to the behaviour towards water and ether, and finally each sub-group into acids, phenols, bases and neutral substances. Such a scheme has obvious advantages, though it is easy to imagine that a substance might turn up in two of the ultimate divisions, because its properties happen to fall along the arbitrary boundary-line dividing two of the sub-groups. But doubtless the author has allowed for this possibility.

The book is furnished with a good index of substances, but not with an index of reactions. This is unfortunate, as the preparation of derivatives is a particularly strong feature of the book, and the absence of an index renders reference to these a troublesome matter.

F. A. ROBINSON

Publications Received

CRYSTAL CHEMISTRY. By R. C. EVANS. Pp. xi + 388. Cambridge University Press. 1939. Price 18s. net.

ORGANIC SYNTHESES. J. R. JOHNSON, Editor-in-Chief. Vol. XIX. Pp. 105. New York: Wiley & Sons. London: Chapman & Hall, Ltd. 1939. Price 8s. 6d. net.

ESSENTIALS OF PHYSIOLOGICAL CHEMISTRY. By A. K. ANDERSON. Pp. xi + 323. London: Chapman & Hall, Ltd. 1939. Price 13s. 6d. net.

USES AND APPLICATIONS OF CHEMICAL AND RELATED MATERIALS. By T. C. GREGORY .Pp. vi + 665. New York: Rheinhold Publishing Co. London: Chapman & Hall, Ltd. 1939. Price 50s. net.

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. 4th Ed. Vol. III.—Chemical Calculations—Diffusion. Pp. xxiii + 608. London: Longmans, Green & Co. Ltd. 1939. Price 63s. net.

LAVOISIER. By J. A. COCHRANE. Pp. 264. London: Constable & Co., Ltd. Re-issue. Price 3s. 6d. net.

A LABORATORY MANUAL OF QUALITATIVE ANALYSIS. By J. H. YOE. Pp. 219. New York: Wiley & Sons. London: Chapman & Hall, Ltd. Price 12s. 6d. net.

THE WAR GASES: CHEMISTRY AND ANALYSIS. By MARIO SARTORI. Translated from the Second Italian Edition by L. W. MARRISON. Pp. xii + 360. London: J. & A. Churchill, Ltd. 1939. Price 21s.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

THE following candidates have been elected members of the Society:

- Douglas Onslow Burgess, Analytical Chemist and Assayer to Messrs. Murex, Ltd., Essex.
- Victor Carcamo Marquez, D.Sc. (Lima), Public Analyst for the City of Lima, Peru.
- John Kay, Analytical and Works Chemist to the Scottish Co-operative Wholesale Society, Glasgow. (*Through the Scottish Section.*)
- Charles Alexander MacDonald, B.Sc. (Lond.), F.I.C., Senior Chemist at Evans' Biological Institute, Runcorn, Cheshire.
- Anavamuda Srinivasan, M.A. (Madras), Chemist at the Indian Government Store Department, London.

- Arif Alamiddin, B.A. (Amer. Univ., Beirut), Government Central Laboratories, Jerusalem.
- Peter Clarke, B.A. (Oxon.), Analyst and Works Manager.
- Abdul-Razzak Dabbagh, B.A. (Amer. Univ., Beirut), Government Laboratory, Baghdad, Iraq.
- Hans Leo Lehmann, Ph.D. (Heidelberg), Analytical Chemist in practice in London.
- Richard William Morris, B.Sc. (Lond.), A.C.G.F.C., D.I.C., F.I.C., Chief Chemist to Messrs. Pearce, Duff & Co., Ltd.
- Harold Sidney Young, B.Sc. (Lond.), A.I.C., Chief Chemist, Messrs. C. & E. Morton, Food Manufacturers.
- Tawfig Iskander Zakharia, B.A. and B.Sc. (Amer. Univ., Beirut), Government Central Laboratories, Jerusalem.

Death

WITH deep regret we record the death of Sir William Pope. An obituary notice will be published later.

Obituary

HENRY TURNER LEA

HENRY TURNER LEA was born at Burton-on-Trent on September 10th, 1889. He was educated at Burton Grammar School, Wellington College, and Birmingham University, where he graduated in science and later obtained the M.Sc. degree. He became an Associate of the Institute of Chemistry in 1917, and was elected to the Fellowship in 1925.

On leaving the University in 1912 he served in the Government Laboratory until 1915, when he joined the Special Brigade of the Royal Engineers. While serving in the ranks he was gassed, and when he resumed duty he was promoted to the rank of Lieutenant and put in charge of the Gas School at Bethune.

In 1919 he took over the consulting practice of Dewhirst of Halifax and succeeded him as Public Analyst. Later he obtained other public appointments, becoming Public Analyst for Scarborough, Huddersfield and Burton-on-Trent.

He joined our Society in 1919 and served on the Council in 1926–7. He also took an active part in the formation of the Northern Section of the Society and, as its first Honorary Secretary, did much to promote its success.

The outstanding characteristic of Lea's personality was his abundant energy, for, in addition to enlarging and extending his practice, he was always ready to accept a responsible position in the many social organisations to which he belonged. He was, for instance, an enthusiastic member of the Halifax Thespians, and produced several successful plays.

He was for many years Honorary Secretary of Queen's Lawn Tennis Club, Halifax, and became an official referee of the Lawn Tennis Association. These and other social activities made for him many friends, by whom he will be greatly missed.

His direct and outspoken manner was appreciated by his clients, who admired his ability to cover his scientific knowledge with what the business man regards as common sense, and this contributed in no small measure to his professional success in the West Riding.

He enjoyed excellent health until a week before his death, which occurred on July 28th during what was thought to be a minor operation.

He married Miss Margaret A. Walsh of Halifax, and she and two children survive him.

At the funeral the Society was represented by the writer, and the Northern Section by Mr. C. H. Manley and Mr. J. Firth.

H. M. MASON

Silicosis and the Analyst

BY F. S. FOWWEATHER, M.Sc., F.I.C., M.D., M.R.C.P., D.P.H.

(*Read at the Meeting of the North of England Section, March 25, 1939*)

IF a person comes in contact with a toxic substance as a consequence of his employment, he runs an "occupational" risk of contracting the disease to which this substance may give rise; should he become incapacitated by the disease he may be entitled to compensation, or his relatives may be entitled to compensation if the disease should contribute to his death.

In examining claims for compensation use is sometimes made of chemical evidence, and analysts are sometimes asked to determine the amount of silica in the lungs of possible victims of silicosis, in the belief that this would be of value in attempting to reach a correct diagnosis in such cases and to deal fairly with the question of compensation. It is of some importance to examine the relation between silicosis and the silica-content of the lungs of its victims in order to see how far this belief is justified, and that examination is the chief object of the present communication.

Silicosis usually runs a chronic course, and rarely makes its appearance until exposure to the dust has continued for a prolonged period. (In Rand gold-miners, for example, the average duration of work before the earliest detectable signs is 13 years.) The first symptom to make its appearance is dyspnoea. This is slight at first, and only becomes evident after prolonged or severe exertion. It is, however, progressive, and later comes to dominate the clinical picture; radiographs at this stage show some areas with discrete shadows. Gradually dyspnoea and cough increase, and physical signs become more definite; radiographs show increased shadows, with a tendency for some to coalesce and exhibit mottling.

Later still there is serious or total incapacity through intensification of symptoms, particularly dyspnoea. The radiograph then usually shows extensive, dense shadows, indicating massive consolidation.

Any other disease accompanying the silicosis may, of course, modify the symptoms, signs, radiographic appearances, and general course of the disease, and the most frequent accompaniment is pulmonary tuberculosis.

The changes in the lungs, which are the cause of the signs and symptoms just described, are the gradual development of areas of fibrous tissue, ultimately quite hard and dense, which take the place of the actively-functioning, more highly specialised, spongy lung tissue. In fatal cases of uncomplicated silicosis the lungs are generally large and of increased density, and generally show some pleural adhesions. On section they very frequently show numerous rounded nodules, which give a characteristic "shotty feel" to the lung tissue. The nodules are dense and tough and composed of fibrous tissue. They may be quite small (2–5 mm. in diameter) or many may coalesce to form larger, composite nodules. The nodules are most abundant in the upper and middle portions of the lung. Some cases show quite massive, fused areas of fibrosis, still retaining evidence, however, of the original nodular character, while others show a still more diffuse and uniform type of fibrosis.

In mild cases of silicosis (seen for example in workers exposed to silica dust who have died from some entirely unrelated disease) changes may be limited to fibrotic areas in the lymphatic glands near the hilum of the lungs, or there may be a few small scattered nodules in the lung substance, often immediately beneath the pleura; between this and the fully developed stage of the fatal case, all grades are possible.

In presence of tuberculosis the typical appearances found in silicosis are modified, sometimes to a very considerable degree, so that, in some cases, the recognition of silicosis, in presence of extensive tuberculosis, may be extremely difficult.

The principal occupations in which silicosis occurs are:

1. *Coal-mining.*—The incidence of the disease varies greatly in the different coal-fields, depending largely on the nature of the rock in which the coal seams lie. South Wales has the greatest incidence among the coal-fields of Great Britain. Silicosis in coal-miners must be distinguished from anthracosis, which is due simply to the accumulation of fine coal-dust in the lungs. This causes only relatively slight and non-progressive fibrosis and, if unaccompanied by silicosis, is a practically harmless condition; it does not appear to cause increased susceptibility to tuberculosis.

2. *Gold-mining.*—Though silicosis from this cause may be contracted in the mines of South Africa or Australia, it has some relevance to the incidence of silicosis in this country, on account of cases among miners who have gone to work in these gold-mines for a time, and then returned home suffering from the disease.

3. *Sand-blasting.*—Here the dust inhaled is almost pure silica, in a finely divided form. According to the Chief Inspector of Factories and Workshops,[1] "No other silicosis-producing industry shows such grave figures for the average working lifetime of fatal cases, or figures comparable to the sand-blasting trade, except the manufacture of scouring powders."

4. *Pottery manufacture.*—Here, of course, the risk occurs only in certain processes; the later processes of decoration and glazing, for example, are free from the risk.

5. *Sandstone industry.*—This includes the quarrying or mining of sandstones, and hence affects quarrymen, and also the preparing and dressing of such stones, which involves stonemasons.

6. *Grinding of metals.*—The risk to the grinder arises where grindstones composed of natural sandstones are used. In many instances the incidence has been reduced by the substitution of artificial abrasive wheels.

7. *Tin-mining.*—A number of cases have arisen in the Cornish industry.

8. *Iron-ore mining.*—Some cases have occurred in the haematite mines of West Cumberland and elsewhere.

9. *The refractories industries.*

10. *Manufacture of abrasive soaps.*—Here highly siliceous material is mixed with powdered soap, anhydrous sodium carbonate, and sometimes other substances. The silicosis risk was not at first appreciated, but the occurrence of a few rapid

and severe cases of the disease soon called attention to it. I have previously referred to a case in which the death of a worker in this industry occurred after only three years' exposure, followed by a three-year period of illness.[2]

The condition arising sometimes in workers with asbestos—called asbestosis—differs from silicosis in certain important respects. In all the industries giving rise to silicosis some part at least of the inhaled dust consists of free silica, whereas the dust giving rise to asbestosis consists of chemically combined silica—principally as magnesium silicate; moreover, the material is of finely fibrous structure, and much of the dust given off from asbestos in process of manufacture consists of fragments of fibres. The clinical condition does not differ greatly from silicosis; dyspnoea is the earliest symptom and the most striking, and gradually increases as the disease progresses. The cause is again a fibrosis of the lungs, but with definite differences from that in typical silicosis. Thus while the fibrosis of the latter is mainly nodular, that of asbestosis is diffuse. Pleural adhesions in asbestosis are usually extensive and dense, especially at the base.

Thickening of the pleura is often a marked feature. The consistence of the whole lung is increased and large areas may show fibrous condensation of a decidedly tough nature.

Asbestosis is in general of more rapid onset than silicosis, the length of time which may elapse between exposure to the dust and a fatal termination being much less than in the average case of silicosis. The incidence of tuberculosis is high, though significantly less than in silicosis.

Having in mind some of the general facts relating to silicosis (and asbestosis), we can now pass on to a consideration of the diagnosis and the part played by chemical analysis. The diagnosis of silicosis and asbestosis during life is a matter for the physician, assisted by the radiologist; the analyst can rarely take any part. It is true that of the silica deposited in the lungs of sufferers, a portion is dissolved by the body fluids, passes to the blood stream and is excreted, but this is an extremely slow process, and its effect on the silica-content of blood and urine is small. A certain amount of silica is ingested with food and later excreted; in blood and urine changes in concentration resulting from ingested silica quite overshadow the changes caused by solution of inhaled silica. This is not simply a matter of probability; it has been the subject of investigation. King and Stantial[3] published a method for the determination of silica in blood and urine, and King and other collaborators have used this method in various experimental studies.

From these it appears that, under certain conditions which cause large increases in the concentration of urinary silica, no marked increase in the silica-content of the blood was observed. So far as urinary excretion of silica is concerned, King and McGeorge[4] say "Some evidence was obtained that the urinary silica was at a higher level among gold-miners than in a non-mining population, but the urinary silica values were found to be so dependent on the nature of the diet that no conclusions could be drawn in single cases."

Occasionally analysts have been asked to determine the silica-content of rock or other material worked by a patient, with a view to showing that he has been subjected to a harmful dust. This, of course, helps hardly at all in the matter of diagnosis; it merely shows whether the occupation is, or is not, a possible cause of silicosis. Moreover, the silica-content alone is not the only factor; the size of the dust particle is of considerable importance, for it is generally agreed that the great majority of dust particles which find their way into the lung are less than 5μ in diameter, and very few exceed 10μ (with fibrous minerals, however, the *length* of fibres found in the lungs may greatly exceed 10μ).

In asbestosis there is one other finding that is of interest, *viz.* the presence of "asbestosis bodies" in the sputum. These are spindle-shaped structures with slender centres and bulbous extremities and vary in length up to 50 or 100μ, though some are much shorter. Many resemble close-set strings of beads, whilst others are apparently unsegmented. The colour varies from faint yellowish-green to deep brown. A fine, transparent asbestos fibre runs through the core of each body. "The bodies are readily demonstrated in the sputum of asbestos workers, at least after the first year or two of employment. In older workers they may be present in profusion, and are best demonstrated by the use of an antiformin concentration method. Their presence is not necessarily an indication that pulmonary fibrosis exists; they merely show that asbestos dust has been inhaled into the lungs and has remained there for some time. The presence of clumps of bodies in the sputum is a much more significant finding, pointing, as it does, to disintegration of lung tissue, whether of tuberculous or simple broncho-pneumonic nature" (Stewart[5]).

CHEMICAL AND PATHOLOGICAL DIAGNOSIS.—The diagnosis of silicosis after death is apparently of more importance to the analyst. Here let me point out that it does not follow that methods that have been useful in the scientific investigation of a condition, and in the elucidation of many important facts concerning it, will continue to be of similar usefulness after these facts have become clearly established; in other words, methods used in investigation may not be of equal value—may in fact be rarely needed—in matters concerned with routine diagnosis of individual cases. This should be quite obvious, yet I find that it is sometimes overlooked.

I believe that lung analyses, in cases of silicosis, have sometimes been asked for by someone who knows that such analyses have been used in the investigation of some of the problems of silicosis, and therefore thinks that they have an application in the consideration of each individual case. This is, in fact, only rarely true. It cannot be too strongly emphasised that the diagnosis of silicosis (and also of asbestosis) after death is essentially made on pathological, not chemical, grounds.

Silicosis is a disease, as we have seen, due to a pathological condition of the lungs. This, it is true, is caused by siliceous material, but unless it can be shown that the amount of silica to be found in the lungs, and the degree of pathological change maintain a reasonably constant relationship, chemical analysis of the lungs can never be a deciding factor in diagnosis. At best, all it can do is to provide certain additional evidence which, in cases where purely pathological evidence is doubtful, *may* possibly help to clarify the issue. We must therefore examine the evidence dealing with the relation between silica-content of lungs, and degree of silicotic fibrosis.

RELATION BETWEEN SILICA-CONTENT OF LUNGS AND FIBROSIS.—Certain general considerations suggest that the relationship is far from close, *viz.*

(1) Not all workers in the dangerous trades contract the disease, *i.e.* many who must have inhaled silica-containing dust, and who must therefore have an appreciable amount of silica in the lungs, do not get clinical silicosis.

(2) Some occupations are more dangerous than others, and this, not because the actual amount of silica inhaled is greater in the more dangerous trade, but presumably because of the nature of the inhaled material. Silicosis is believed to be due to a chemical and not to a physical action of silica; hence factors concerned with degree of chemical reactivity, *e.g.* particle size, may be, and almost certainly are, of much more importance than total quantity of silica.

(3) The great variability in reaction of the human body to toxic substances is well-known. A dose of a poison sufficient to cause death in one individual may cause little disturbance in another, and there is no reason to believe the reaction of the human body towards silica to be more constant than its reaction to most other harmful agents.

But we need not rely on general considerations only, since more precise facts are at our disposal. In considering these it is well to have in mind some figures relating to the silica in normal lungs. The cases I have personally been concerned with show values up to 0·20 per cent. (on the weight of dried lung) and most other investigators have obtained similar figures.

In a number of cases dealt with by Professor Stewart and myself, different portions of lungs from the same individual, showing different degrees of silicotic fibrosis, have been analysed separately. Even here, where the same dust has operated in the same individual, the correlation between amount of silica and degree of fibrosis is not a very close one. While, in general, the more fibrotic portion has been found to contain more silica than the less fibrotic portion, great differences between degrees of fibrosis have sometimes been found where differences in silica-content were relatively small, and *vice-versa.* A few examples will illustrate this:

(1) A portion of lungs showing massive, nodular silicosis contained 2·62 per cent. of silica, whilst the rest of the lungs, showing silicosis to a considerably less degree, contained 2·00 per cent.

(2) Portions of lungs which were densely silico-anthracotic contained 5·04 per cent. of silica, whilst portions with so little fibrosis as to justify the description of spongy, contained 2·22 per cent. In contrast with this—

(3) Portions of lung grossly silicotic contained 2·66 per cent. of silica, while spongy portions contained 0·33 per cent.

(4) In lungs with fairly widespread changes, the more silicotic portions contained 1·14 per cent. of silica, whilst the less silicotic (but not spongy) portions contained 0·28 per cent.

(5) In a case of very advanced silicosis the densely fibrotic portion contained 0·94 per cent. of silica, whilst portions that were less fibrotic, but contained scattered, dense nodules showed only 0·21 per cent.—practically a normal figure.

When we come to compare the lungs of different individuals, in different occupations, the lack of correlation between silica-content and degree of fibrosis is often very striking. I do not propose to quote figures on this point, as I have already done so elsewhere[3] some time ago.

Since these figures were obtained many more analyses have been carried out, but these have not yet been fully examined. They include, however, sufficient figures for certain specific industries to allow of some comparisons between lungs of different individuals in the same occupation. It is probable that when they have been properly studied they will show a closer correspondence between silica-content and degree of fibrosis than where cases in different occupations are considered, but I have little doubt that here, too, this correspondence will prove to be only a very rough one.

It is true, of course, that the majority of silicotic lungs that have been examined show an increased silica-content. Hence, in a general way, it might be said that the finding of increased silica in lungs indicates the probability that silicosis may be present, and the degree of probability depends on the amount by which this increased silica exceeds the normal. But it is difficult to state any limiting figure beyond which it might be said that the probability becomes a certainty. Thus, in our own experience most lungs containing 1 per cent. or more of silica have been found to be silicotic, yet we have come across two or three cases with figures in the neighbourhood of 2 per cent. which showed little or no silicosis, and in one case in which the lungs contained over 6 per cent. of silica, there was only a moderate degree of fibrosis.

It must be remembered, too, that while many cases of silicosis are subjected to post-mortem examination, few cases of those in the same occupations who die of some cause having no obvious relation to silicosis receive such examination. So far as our own work is concerned, we have received material from cases of silicosis from various sources, while for material from cases without silicosis but with a silicosis risk we have been restricted to patients who have died in the Leeds General Infirmary, whose history has indicated an employment in a dangerous occupation. Our knowledge, therefore, of the amount of silica to be found in lungs of such cases is from a much smaller sample of the persons concerned, than of those suffering from silicosis, and is consequently much less complete. It is therefore possible that the number of cases of high lung silica, with little or no silicosis, is higher than the figures at present available indicate.

Again, the finding of a normal lung silica value does not with certainty establish the absence of silicosis, but only the probability of such absence. This is particularly true of asbestosis.

In considering the bearing of analytical results on any particular case, it is always desirable to take into account also as much evidence as can be obtained regarding the nature of the occupation, its duration, and the length of time which has elapsed between giving up the occupation and death.

EVIDENCE OF SILICOSIS.—In the majority of cases of possible silicosis which come up for consideration there is no difficulty in arriving at a true appreciation of the condition; there is clear pathological evidence of silicosis and a history of exposure to a harmful dust, usually over a considerable period of time. In cases where the degree of silicosis does not appear of itself to be the cause of death, and some other disease is also present, the question as to whether the silicosis is a contributory cause of death is to be decided on a consideration of all the pathological evidence obtainable, together with, in some cases, the clinical evidence; chemical evidence is of little value.

The presence of tuberculosis sometimes raises difficulties. Fibrosis of the lung *per se* is not a reaction specific to silica; it is an accompaniment of most chronic diseases, and this is especially true of the more chronic forms of tuberculosis.

In many cases there is clear evidence of both silicosis and tuberculosis. Difficulties only arise where it may be impossible to decide whether silicosis is actually present or not. In such cases the history is of considerable importance, and where it clearly establishes exposure to a harmful dust (*i.e.* occupation in a dangerous trade), it will have very considerable influence on the final decision. Where the history is inconclusive, chemical analysis, if it establishes proof of exposure to a harmful dust, will become an important factor.

In the absence of tuberculosis, cases sometimes show some lung fibrosis, which though not characteristically of silicotic type, may be considered to be probably due to the action of silica; here, too, evidence regarding exposure is important. Chemical analysis may afford proof of exposure and also instigate a more careful investigation into the past history.

In doubtful cases, whether tuberculous or not, the possibility, on pathological grounds, that the condition may be silicotic, together with adequate proof of sufficient exposure to a harmful dust, will, as a rule, be accepted as sufficient grounds for establishing a claim for the condition to be considered as one of silicosis. For compensation purposes, at any rate, chemical analysis, apart from its bearing on the question of exposure, will very rarely be called for. From a more scientific point of view, the information obtainable from chemical analysis would probably justify consideration more frequently.

CHEMICAL EVIDENCE.—It will be realised from what has already been said, that the analyst can give very little help in the great majority of cases of silicosis; so far as the remainder are concerned, the object of his work will mainly be to supply evidence concerning exposure to a dangerous dust. One case in which analysis proved of considerable interest in this respect seems worth recording. During the examination of what were believed to be lungs from normal individuals, one case, that of a man described as a labourer, gave a figure for lung silica of 0·45 per cent. As this figure is more than double what had been found in other normal cases, it indicated, either that the normal range was greater than had previously been thought to be the case, or that the labourer had been exposed to a siliceous dust. A more careful examination of the history was therefore made, and it was proved that the man had been employed as a packer with the Leeds Fireclay Co. He was therefore not a "normal" from the point of view of exposure to dust, though his lungs showed no fibrosis.

Occasionally cases of silicosis arise in connection with occupations not normally considered to be dangerous from this point of view. One such case is reported by Edwards.[6] It concerns a grave-digger who died, after 17 years at this occupation, of what was believed at first to be tuberculosis; an expert, however, considered the case to be one of silico-tuberculosis. Unfortunately no analysis of the lungs was made. It was found, however, that the graves dug by the man were in red sandstone, and pneumatic drills were often employed. The job was a very dusty one, particularly in dry weather. There was therefore clear evidence here of exposure to a dangerous dust. It is conceivable, however, that in some unusual cases, evidence of such exposure may depend on chemical analysis.

ANALYSIS OF LUNGS.—The method I have used for the analysis of lungs is on orthodox lines, and is not original. The specimen is cut up into pieces about half-an-inch in diameter, with scissors, and dried for three or four days in the steam-oven. It is then ground in an iron mortar to pass a 30-mesh sieve. Four g. are weighed into a platinum dish (5 × 2 cm.), or 3 g. if a high silica-content is expected, and the ash is determined, heating being at first carried out carefully over a small Bunsen flame until charring is complete, and then in a Davies crucible furnace heated with a Heinz burner.* After the weight of the ash has been determined, 12 to 15 times that weight of fusion mixture (equal parts of sodium and potassium carbonates) is added in the dish, and the mixture is fused in the furnace for 2½ hours.

After cooling, the fused substance is dissolved in 20 per cent. hydrochloric acid (*i.e.* 1 part of conc. hydrochloric acid to 4 parts of water), and the solution is evaporated to dryness in a porcelain dish on the water-bath. A further 20 ml. of 20 per cent. hydrochloric acid are added, and the mixture is again evaporated to dryness. The residue is then baked in an air-oven at 110° C. for from 30 mins. to an hour. The dish is cooled slightly, 1 ml. of conc. hydrochloric acid and 19 ml. of hot water are added, the dish is placed on a water-bath, and, after digesting for about 15 minutes, the contents are filtered through a No. 44 Whatman filter-paper. The filtrate and washings are evaporated to dryness, a further 20 ml. of 20 per cent. hydrochloric acid are added, and the liquid is again evaporated to dryness. The residue is baked, as before, at 110° C., treated with 1 ml. of hydrochloric acid and 19 ml. of hot water, allowed to simmer, and filtered through a second filter-paper. The two filter-papers are burnt together in a second platinum dish, and the residue is heated on the furnace for an hour, after which the residue of crude silica is weighed.

To this crude silica 1 ml. of water and 0·2 ml. of conc. sulphuric acid are added, and then 5 ml. of pure hydrofluoric acid, and the mixture is evaporated on the water-bath until only sulphuric acid is left. If necessary, a further 2 ml. of hydrofluoric acid are added and the mixture is again evaporated. Finally the remaining sulphuric acid is carefully driven off over a free flame, and the residue is then heated for half-an-hour in the furnace. The weight of the residue gives the amount of material not volatilised with hydrofluoric acid, and this is subtracted from the crude silica to give the weight of pure silica.

The platinum dish used for the incineration and fusion of the ash is attacked somewhat in the process, and after it has been used for a few times there is a tendency for scaling to occur. It is advisable, therefore, to scrape the inner surface after each fusion to remove such scale. I find that 60 to 70 incinerations and fusions can be carried out before it is necessary to renew the dish (at a cost of about one pound). Dr. Faulds (personal communication) has used stainless steel dishes for this part of the process, and finds them satisfactory.

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* The Davies furnace, as supplied by Messrs. Gallenkamp & Co., is heated with a Teclu burner, but the Heinz burner (of foreign make) is more satisfactory.

Colorimetric micro-methods for silica determination are also in use. King and Stantial,[3] for example, give methods for determining silica in blood, urine and tissues, the basis being the production of a yellow silico-molybdic acid complex, and the reduction of this to give a blue colour. For details of the method the original paper should be consulted.

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The Determination of Manganese by means of 8-Hydroxyquinoline in Presence of Magnesium

BY G. STANLEY SMITH, B.Sc., A.I.C.

BERG[1] precipitated manganese as the hydroxyquinoline complex, $Mn(C_9H_6ON)_2$, $2H_2O$, from solutions faintly acid with acetic acid, or faintly ammoniacal, and obtained by either method a satisfactory separation from the alkaline earths, though not from magnesium.

Separation from magnesium, if possible, would be of importance, particularly since magnesium is the element most frequently determined by the hydroxyquinoline method.[2]

According to Gotô,[3] the reagent precipitates manganese, quantitatively in the *p*H range, 5·87 to 10·00, partially at *p*H 4·55 and 12·32, and not at all at *p*H 4·25. Hence, unless co-precipitation is unavoidable, a separation of manganese from magnesium, which is precipitated above *p*H 7, should, presumably, be possible.

The method for aluminium which I described recently[4] has now been applied to the determination of manganese. It appears from the results of the investigation detailed below, that, whilst moderately small amounts of magnesium (0·01 g.), cause no appreciable interference, amounts of the order 0·1 to 0·5 g. cannot be separated with certainty unless the manganese precipitation is repeated.

Except for other details shown later, the method followed that for aluminium. The manganese solution, prepared by reducing a permanganate solution with hydrogen peroxide in presence of dilute sulphuric acid and boiling off the excess of peroxide, was treated with 8-hydroxyquinoline solution (3 per cent. in 0·2 *N* hydrochloric acid), and dilute ammonia solution was added, drop by drop, to the nearly boiling solution until a cloudiness remained. A known volume of *N* hydrochloric acid was added, and then 10 ml. of the acidity-regulating solution (28 g. of potassium bromate, 120 g. of potassium bromide and 250 g. of sodium thiosulphate per litre), the solution (100 to 110 ml.) was boiled for exactly one minute and filtered, and the precipitate was washed with hot water and dissolved in hydrochloric acid (30 ml. of concentrated acid with 90 ml. of water). The solution was cooled,

TABLE I

Manganese mg.	Magnesium g.	Hydroxyquinoline 3 per cent. ml.	Hydroxylamine hydrochloride g.	Hydrochloric acid, N ml.	Bromine, 0·1 N reqd. ml.	Bromine, 0·1 N calc. ml.
27·5	—	10	0·025	2	41·05	40·05
22·0	—	10	0·025	2	32·35	32·04
					32·35	32·04
16·5	—	10	0·025	2	24·5	24·03
27·5	—	6	0·025	2	40·4	40·05
16·5	—	4	0·025	2	23·7	24·03
11·0	0·5	6	0·025	3	17·7	16·02
11·0	0·1	6	0·05	2	17·7	16·02
16·5	—	6	0·1	3	24·05	24·03
27·5	—	6	0·1	3	37·75	40·05
27·5	0·2	6	0·2	2	35·8	40·05
27·5	—	7·5	0·2	1	39·4	40·05
27·5	—	7·5	0·1	1	39·95	40·05
27·5	0·4	7·5	0·1	1	40·65	40·05
22·0	—	10	0·1	1	32·55	32·04
5·5	—	6	0·1	2	8·15	8·01
5·5	0·2	6	0·1	2	13·2	8·01
16·5	0·2	6	0·1	2	25·25	24·03
5·5	—	6	0·1	4	8·0	8·01
					7·85	8·01
5·5	—	6	0·1	5	6·25	8·01
27·5	—	10	0·02	3	40·7	40·05
27·5	0·1	10	0·02	3	39·3	40·05
					40·75	40·05
27·5	0·1	6	0·02	3	32·8	40·05
27·5	0·1	10	0·02	2·5	41·0	40·05
					42·0	40·05
27·5	—	10	0·02	1	40·6	40·05
27·5	0·2	10	0·02	2	40·9	40·05
5·5	0·1	10	0·01	3	9·15	8·01
16·5	0·1	10	0·01	3	25·0	24·03
5·5	0·1	10	0·01	4	8·8	8·01
16·5	0·	10	0·01	4	25·0	24·03
5·5	0·	10	0·01	5	7·6	8·01
16·5	0·	10	0·01	5	23·7	24·03
16·5	0·	10	0·01	5	24·25	24·03
16·5	0·	10	0·01	4·5	24·3	24·03
16·5	—	10	0·01	6	20·85	24·03

0·1 N bromine solution (2·805 g. of potassium bromate, 12 g. of potassium bromide and 25 ml. of 0·5 per cent. indigo carmine solution per litre) were added in small excess, and the excess was determined by back-titration with 0·1 N thiosulphate solution, after addition of potassium iodide and finally starch.

One ml. of 0·1 *N* bromine ≡ 0·6866 mg. of manganese.

The figures shown below for ml. of 0·1 *N* bromine solution required represent the volume actually used, less the volume of thiosulphate solution required in the back-titration. Magnesium, when included in the solution with the manganese, was added as the chloride.

The following modifications of the method were tried:

(1) The manganese solution, containing 10 ml. of hydroxyquinoline reagent, nearly boiling, was treated with weak ammonia until one drop produced a cloudiness, and then boiled for one minute with the "buffer" solution.

Mn, 22·0 mg.; Mg, nil; 0·1 *N* bromine, 32·6, 32·65, 32·5 (calc., 32·04).
Mn, 22·0 mg.; Mg, 0·01 g.; 0·1 *N* bromine, 36·6, 35·1 (calc. 32·04).

These precipitates were of a brown colour, possibly owing to the presence of manganese in a higher state of oxidation. Berg used sulphur dioxide or hydroxylamine to reduce manganese to the bivalent state before precipitation.

(2) A few drops of sulphur dioxide solution were added before the ammonia; 3 ml. of *N* hydrochloric acid were added on the appearance of cloudiness produced by ammonia.

Mn, 16·5 mg.; Mg, nil; 0·1 *N* bromine, 24·6 (calc., 24·03); brown ppt.
Mn, 16·5 mg.; Mg, 0·5 g.; 0·1 *N* bromine, 25·05; yellow ppt.

(3) In the experiments (Table I), p. 788, hydroxylamine hydrochloride was added to the manganese solution with the hydroxyquinoline. Ammonia solution (approximately 2 *N*) was dropped into the nearly boiling solution until a cloudiness appeared, *N* hydrochloric acid was added in the amounts shown on p. 788, and then, after a short period of boiling, 10 ml. of the "buffer."

TABLE II

Manganese mg.	Magnesium g.	Hydroxyquinoline, 3 per cent. ml.	Hydrochloric acid, *N* ml.	Bromine, 0·1 *N*	
				reqd. ml.	calc. ml.
16·5	—	6	3	24·3	24·03
16·5	0·1	6	3	25·15	24·03
16·5	—	10	3	24·0	24·03
				24·2	24·03
				24·1	24·03
16·5	0·1	10	3	25·2	24·03
16·5	0·01	10	3	24·2	24·03
22·0	0·002	10	3	32·15	32·04
22·0	0·01	10	3	32·2	32·04
22·0	—	10	5	32·0	32·04
22·0	0·1	10	5	33·4	32·04

The precipitates obtained in presence of hydroxylamine were yellow when magnesium was absent. The colours tended to be greenish-yellow, sometimes a decided green, when magnesium was present, and the filtrates were also more or less green.

(4) In the above experiments (Table II) the solution before the precipitation contained ammonium chloride equivalent to 10 ml. of conc. hydrochloric acid. No sulphur dioxide or hydroxylamine was added, but the acid solution was

boiled for several minutes immediately before the introduction of the "buffer" solution.

All the precipitates were pale yellow, but they tended to clog the filter, making filtration somewhat slower than in absence of ammonium chloride.

(5) Hydrogen peroxide was added immediately before the "buffer" solution. Ten ml. of 3 per cent. hydroxyquinoline solution were present in each experiment (Table III).

TABLE III

Manganese mg.	Magnesium g.	Hydrogen peroxide) (20 vol.) ml.	Hydrochloric acid, N ml.	Bromine, 0·1 N reqd. ml.	Bromine, 0·1 N calc. ml.
5·5	—	1	3	8·1	8·01
5·5	0·2	1	3	14·3	8·01
22·0	0·4	1	4	34·2	32·04
22·0	—	2	3	32·35	32·04
5·5	—	2	5	8·15	8·01
5·5	0·5	2	5	11·7	8·01
16·5	2·0	2	4	25·1	24·03
16·5	0·5	2	5	30·4	24·03

All these precipitates were yellow, and could be filtered off rapidly.

(6) Ammonium chloride present equivalent to 10 ml. of conc. hydrochloric acid. Hydrogen peroxide (1 ml. of 20 vol.) was added, and the solution was boiled for about one minute before the "buffer" solution was added. Ten ml. of hydroxyquinoline solution were present in each experiment (Table IV).

TABLE IV

Manganese mg.	Magnesium g.	Hydrochloric acid, N ml.	Bromine, 0·1 N reqd. ml.	Bromine, 0·1 N calc. ml.
16·5	—	4	24·1	24·03
16·5	—	5	24·0	24·03
16·5	0·01	4	24·05	24·03
16·5	0·025	5	24·35	24·03
27·5	0·05	5	40·3	40·05
27·5	0·5	5	42·7	40·05

These precipitates were yellow and readily filterable. It is important not to boil the manganese solution containing both hydroxyquinoline and hydrogen peroxide for several minutes, as a deep brown solution results, from which the "buffer" solution throws down a sticky brown precipitate, whether ammonium chloride is present or not.

The method recommended for the precipitation is No. 6 above, followed by a re-precipitation under the same conditions if the magnesium exceeds 0·10 g. The manganese solution (about 100 ml.), nearly boiling, and containing about 6 g. of ammonium chloride or 10 ml. of conc. hydrochloric acid and 10 ml. of the hydroxyquinoline reagent, is neutralised with ammonia solution (finally with 2 N ammonia) until a permanent precipitate appears. Hydrochloric acid (4 or 5 ml. of an N solution) and a few drops of hydrogen peroxide are then added, the solution is boiled, 10 ml. of the "buffer" solution are added, boiling is continued for exactly one minute, and the solution is filtered.

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* NOTE.—In studies of hydroxyquinoline precipitations Gotô's results are of interest. A summary is given below.

*p*H RANGES FOR HYDROXYQUINOLINE PRECIPITATIONS, ACCORDING TO H. GOTÔ
(*Sci. Rep. Tôhoku*, 1937, **26**, 391; *ibid.*, 1938, **26**, 418 [Mo and V])

Metal	No ppt. (acid)	Min. *p*H for complete pptn.	Max. *p*H for complete pptn.	No ppt. (alkaline)
Al	2·8	4·2	9·8	12·3
Zn	2·8	4·4	Very great	—
Cd	4·0	5·4	do.	—
Ni	2·8	4·6	10·0	(>13·2)
Mn	4·3	5·9	10·0	(>12·3)
Co	2·8	4·2	11·6	—
Ti	3·5	4·8	8·6	12·0
U	3·1	4·1	8·8	12·1
Th	3·7	4·4	8·8	12·5
Pb	4·8	8·4	12·3	—
Ca	6·1	9·2	Very great	—
Mg	6·7	8·2	do.	—
Fe (ferric)	2·4	2·8	11·2	—
Cu	2·2	2·7	Very great	—
Bi	3·5	4·8	10·5	12·9
Mo	0·7	3·3	7·6	13·1
V	1·1	2·7	6·1	7·3

G. S. S.

The Determination of Ethyl Alcohol in presence of Methyl Alcohol, *iso*Propyl Alcohol and Acetone

BY E. J. BOORMAN, B.SC., PH.D., D.I.C.

METHYL alcohol, *iso*propyl alcohol and acetone are frequently present with ethyl alcohol in modern solvents and lacquers. Since they are not completely removed when the Thorpe and Holmes[1] method for the determination of ethyl alcohol is applied, their presence reduces the specific gravity of the distillates, and consequently increases the apparent proportion of ethyl alcohol present. There is no convenient, rapid, accurate method for the determination of the ethyl alcohol under these conditions. The following work describes such a method.

The preparation of a distillate containing only water and the four compounds mentioned above is normally readily achieved by the method of Thorpe and

Holmes,[1] or by suitable modifications thereof. The presence of methyl alcohol in this distillate may be shown by Simmonds' modification[2] of Denigès' test[3] which, under these conditions, is specific for methyl alcohol; that of acetone by Adams and Nicholls's test,[4] or the iodoform reaction; that of *iso*propyl alcohol by Bodendorf's test.[5] This latter, however, is not specific; a more reliable test is that of Adams and Nicholls[4] (*loc. cit.*) after removal of acetone by methods already known (Hoskins,[7] Hoff and Macoun,[8] Macoun[9]). Ethyl alcohol may be detected by the "aldehyde resin" test of Thresh.[10]

It has been shown by Denigès,[6] and later by Hoskins,[7] that acetone forms an insoluble compound with mercuric sulphate; this reaction may be used to remove small quantities of acetone from aqueous solution. The present method depends on the formation of an analogous compound with mercuric dichromate, which produces a deep orange or red precipitate when an aqueous solution of stoichiometrically equivalent amounts of mercuric sulphate and potassium dichromate is heated to 70–80° C., with acetone. In presence of a large excess of reagent the precipitation of the acetone is quantitative. As sulphuric acid is used to prepare the mercuric sulphate solution, the liquid has strong oxidising properties, and under the conditions of the experiment, *iso*propyl alcohol is oxidised to acetone which, before further oxidation can occur, reacts to form the insoluble mercury dichromate compound. Methyl alcohol is oxidised to carbon dioxide and water, and ethyl alcohol quantitatively to acetic acid. The acetic acid may be distilled in steam and titrated with standard alkali. The compound of acetone appears to be quite unaffected under these conditions, which are such that free acetone would be rapidly oxidised. The nature of the compound has not yet been elucidated, but work on the subject is proceeding.

Methyl ethyl ketone has been found to yield an analogous compound.

WARNING

These mercury chromium compounds, when moist, are stable, but when dry are sensitive to heat or shock and explode violently when struck. They are readily destroyed by conc. hydrochloric acid. It is necessary to emphasise strongly their dangerous character. For this reason, the method described should be used only when others are inconvenient, and then only by skilled workers.

The acetic acid produced by the oxidation of 0·5 ml. of proof spirit is equivalent to 49·5 ml. of $N/10$ alkali. It has been found that 100 ml. of the reagent are capable of retaining acetone equivalent (in sp.gr.) to about 0·7 ml. of proof spirit and of completely oxidising considerably more than this quantity of methyl alcohol. Thus the experiments have been conducted with 100 ml. of reagent and a solution containing a total of not more than 0·55 ml. of apparent proof spirit, for convenience of the volume of steam distillate required and its titre with $N/10$ alkali.

METHOD.—The reagent is prepared by dissolving 100 g. of mercuric oxide in 250 ml. of conc. sulphuric acid diluted with approximately 3 volumes of water and making up to 2 litres with water, in which is dissolved 135·7 g. of potassium dichromate. The distillate resulting from the process of purification already indicated, if of high strength, is diluted to admit of accurate measurement of a suitable volume containing not more than 0·5 ml. of apparent proof spirit, and to this quantity are added 100 ml. of reagent. The whole is allowed to stand at room temperature in a well-stoppered flask for 30 minutes, with occasional agitation. This ensures complete oxidation of the ethyl alcohol. Heating the solution without this preliminary period of cold reaction leads to loss of acetaldehyde. The solution is then boiled under reflux for 15 to 20 minutes. In presence of acetone or *iso*propyl alcohol a heavy precipitate is thrown down at approximately 80° C., and in presence of methyl alcohol carbon dioxide is evolved. This boiling is necessary to drive off any carbon dioxide formed and to ensure completion of oxidation. The flask is then partly cooled, the condenser is rinsed down with water, and the liquid is distilled in steam. The volume may be conveniently reduced to about 75 ml. during the distillation. It has been found that by using slightly alkaline distilled water in the steam generator, the deleterious effect of entrained acid gases on the titration is practically eliminated. Five hundred ml. of distillate are normally sufficient, and are titrated against $N/10$ alkali, phenolphthalein being used. A further 50 ml. is then collected, and should the titre of this exceed 0·1 ml. of $N/10$ alkali, a further 150 ml. are collected and titrated. From the total titre the amount of ethyl alcohol present may be calculated, 1 ml. of $N/10$ alkali being equivalent to 0·0101 ml. of proof spirit.

TABLE I

Ethyl alcohol, as proof spirit ml.	Other ingredient, equivalent as proof spirit ml.	Total apparent proof spirit ml.	Ethyl alcohol found, as proof spirit ml.
0·5185	—	0·5185	0·5175
0·4148	—	0·4148	0·4146
0·3111	—	0·3111	0·3105
0·2074	—	0·2074	0·2072
0·1037	—	0·1037	0·1040
0·0519	—	0·0519	0·0525
	Acetone		
0·4148	0·1037	0·5185	0·4138
0·2074	0·3111	0·5185	0·2070
0·1037	0·4148	0·5185	0·1035
	Methyl alcohol		
0·4148	0·1137	0·5285	0·4145
0·2074	0·3411	0·5485	0·2077
0·1037	0·4548	0·5585	0·1040
	*iso*Propyl alcohol		
0·4148	0·0989	0·5137	0·4140
0·2074	0·2967	0·5041	0·2078
0·1037	0·3956	0·4993	0·1035

RESULTS.—Series of experiments have been made with the single substances as controls; also with mixtures of ethyl alcohol with each of the other compounds singly, and with mixtures of all four. With methyl and *iso*propyl alcohols and acetone alone in quantities up to 0·7 ml. of apparent proof spirit, figures obtained for the distillates (50 ml.) were all less than that equivalent to 0·0005 ml. of proof spirit, whilst with distillates of 500 ml. all were less than that equivalent to 0·0025 ml. of proof spirit.

Table I gives figures for ethyl alcohol alone, and with single added impurities. Table II gives results for four component blends. The fourth place of decimals is given as calculated, although, from the figures quoted, the accuracy of the method is apparently of the order of $\pm 1 \times 10^{-3}$ ml. of proof spirit.

TABLE II

EXPRESSED AS (APPARENT) PROOF SPIRIT

Ethyl alcohol ml.	Methyl alcohol ml.	*iso*Propyl alcohol ml.	Acetone ml.	Total ml.	Ethyl alcohol found ml.
0·0519	0·0828	0·1824	0·2374	0·5545	0·0525
0·1037	0·1592	0·1978	0·0622	0·5229	0·1040
0·2074	0·1024	0·1780	0·0414	0·5292	0·2070
0·4150	0·0456	0·0593	0·0207	0·5406	0·4149
0·0519	0·1656	0·2736	0·0791	0·5702	0·0518
0·1037	0·2276	0·0593	0·1244	0·5150	0·1040
0·2075	0·2048	0·0396	0·0933	0·5452	0·2075
0·4150	0·0684	0·0198	0·0414	0·5446	0·4145
0·0519	0·2484	0·0912	0·1582	0·5497	0·0522
0·1038	0·0684	0·1385	0·2073	0·5180	0·1045
0·2075	0·0456	0·0890	0·1866	0·5287	0·2080
0·4150	0·0228	0·0396	0·0622	0·5396	0·4145

SUMMARY.—Methyl and *iso*propyl alcohols and acetone are removed in one operation from their mixtures with ethyl alcohol. The ethyl alcohol is oxidised quantitatively to acetic acid and estimated as such after distillation in steam from the reaction mixture.

I am indebted to Dr. J. J. Fox, C.B., Government Chemist, for permission to publish this work.

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Extract of Malt with Cod-Liver Oil: Determination of Oil and Vitamin A

BY D. C. GARRATT, B.SC., PH.D., F.I.C.

(*Read at the Meeting, May* 3, 1939)

THE determination of the oil-content of Extract of Malt with Cod-liver Oil, and of the vitamins in the oil, is a matter of considerable importance to buyers who wish to check the quality of this article supplied to them. It appeared to those responsible for approving supplies to the London County Council (as a large user) that the matter required investigation in order to see whether the full quantity and quality of oil admixed in the manufacture could be recovered by any simple process, and hence the rejection be justified of any consignment which, on analysis, was found to be deficient in either respect.

Some methods for determination of oil in this preparation could be traced in the literature, but little work on the vitamin A content of the recovered product has been published.

In preliminary experiments attempts were made to determine the vitamin A content of the extracted oils without making any attempt to obtain quantitative yields of the oil. This procedure subsequently seemed inadvisable, since direct spectrographic determination of $E^{1\%}_{1\text{cm.}}$ $328m\mu$ on the extracted portion gave very high figures, indicating extraction of light-absorbing substances out of proportion to the true $E^{1\%}_{1\text{cm.}}$ $328m\mu$ value of the oil. This is clearly demonstrated by the following results:

TABLE I

		$E^{1\%}_{1\text{cm.}}$ $328m\mu$
(*a*)	Direct extraction of oil with cold ether after "massing" with anhydrous sodium sulphate ..	0·83
	With very small proportionate recovery.. ..	Not less than 1·0
(*b*)	Direct extraction with light petroleum containing ether, after solution in water	0·87
	With very small proportionate recovery.. ..	General absorption
(*c*)	Cod-liver oil used	0·60

It was soon evident that, with the small quantities of oil being handled, relatively large losses of vitamin A could occur during standing and heating, and it was decided that, to avoid unnecessary risk, an extraction in duplicate was desirable, the oil extracted for vitamin A assay being calculated from the gravimetric result. This would minimise possible loss of vitamin A and, incidentally, some oil would be obtained that could be used for determination of the normal constants. The avoidance of the drying and weighing of the oil was considered a particularly necessary innovation for obtaining accurate quantitative vitamin A results; it involved the use of a method which could be relied upon to give reproducible and correct results.

Hence the investigation resolved itself into two problems: (i) the quantitative extraction of oil from the emulsion, (ii) the suitability of the extracted oil for determining vitamin A. Although these problems were investigated together, it will be convenient to consider each separately.

(1) THE QUANTITATIVE EXTRACTION OF OIL FROM EXTRACT OF MALT WITH COD-LIVER OIL.—Several methods for the direct determination of oil in this preparation are known; they mostly appear to be evolved from general methods of fat determination and, with one exception, none published has been based on an investigation to show how closely the recovery of oil compared with the actual quantity present. From time to time I had tried many of these methods and modifications. Those more likely to be successful for full recovery of oil are briefly reviewed below and criticised in view of the requirement that the extracted oil shall contain its original vitamin A content.

(*a*) *The Werner–Schmidt method.*—When this process is used for Extract of Malt with Cod-liver Oil, considerable heating is necessary to break down the emulsion, and the extracted oil is oxidised and quite unsuitable for the determination of the vitamin A content. High results for the oil-content are common.

(*b*) *Extraction with ether or light petroleum in presence of alcohol after some acid hydrolysis.*—Intractable emulsions in the solvent layers are very frequent and low results are common; long periods of standing may be necessary for separations. A modification of this method, involving the use of strong alcoholic solution and extraction with light petroleum, is given by Waggoner and Glover.[1] Large volumes of solvent are required.

(*c*) *Adams' method* (*modified*) *for fat in milk.*—A greatly diluted suspension of the extract is filtered through paper pulp, which is dried and extracted with ether. The method is tedious, and in the drying process the extracted oil is highly oxidised and all vitamin A is destroyed.

(*d*) The preparation is "massed" with anhydrous sodium sulphate until a dry powder is obtained; this is extracted in a Soxhlet apparatus with solvent. Long-continued Soxhlet extraction is necessary to ensure quantitative extraction of the oil. Accurate results appear to be fortuitous.

(*e*) Saponification of the preparation with alcoholic potash, removal of alcohol, acidification and extraction of the fatty acids and unsaponifiable matter. The oil percentage is then obtained by calculation. Considerable exposure of the oil to heat and oxygen is necessary in this method.

The above methods were discarded without trial in this investigation as being almost certain to give either unreliable oil recovery or, where full recovery was expected, low vitamin A figures.

Two methods of assay, *viz.* the Rose–Gottlieb method and the Gunn and Venables[2] method, seemed to offer the best chance of effecting a sharp separation of the oil without unnecessary heating or exposure, and it was decided to concentrate attention on these methods and any modifications of them.

(*f*) *The Rose–Gottlieb method.*—Disperse about 5 g. of the preparation in 5 ml. of water and transfer the mixture to a stoppered 100-ml. tube by means of a further 5 ml. of water. Add 1 ml. of ammonia solution (sp.gr. 0·880) and 5 ml. of alcohol followed by 25 ml. of ether, using part to rinse in any oil possibly remaining in the original weighing vessel. Stopper and shake vigorously for two or three minutes. Add 25 ml. of light petroleum (40°–60° C.) and shake again.

Allow the mixture to stand at least half-an-hour to separate, and syphon off the solvent layer into a tared flask. Repeat twice the shaking and extraction with the ether and light petroleum, using 15- to 20-ml. portions of each for these extractions. Evaporate, re-evaporate after addition of a few ml. of alcohol or acetone, dry and weigh the oil. Different quantities of extract of malt with cod-liver oil give comparable results. When 5-g. quantities are used there is a greater tendency to emulsification, and small quantities, *e.g.* 1 g., are inclined to give somewhat high figures, since slight solubility of malt extractives increases the apparent yield of oil unduly. The following modifications of this method were tried.

(i) *The Society of Public Analysts method*[3] for condensed milk. Results were in agreement.

(ii) The formation of emulsions between the solvent and aqueous layers may often be avoided by heating the aqueous-alcoholic dilution of the sample in a water-bath just to the b.p. of the alcohol, with subsequent cooling before adding ammonia and solvent.

For extract of malt with cod-liver oil such a modification was sometimes found to be helpful and sometimes of no value, or even detrimental—quite at random.

(iii) Stokes' milk tubes (19 × 2·5 cm.), specially made to fit a Gerber centrifuge and holding about 65 ml. of liquid, were successfully adapted for this determination, the quantities of ether and light petroleum each being reduced to 20 ml. for the first extraction, with corresponding reduction in volumes for the second and third extractions. The tubes were centrifuged for two minutes at 1000 r.p.m., and gave sharp separations, so that the time was considerably reduced—a useful point in assaying vitamin A.

Scriba[4] suggested the use of a separator for the Rose–Gottlieb method, but the difficulty of running off the aqueous layer completely makes the manipulation difficult, and the method was discarded.

(*g*) *Gunn and Venables*[2] *method.*—In this method the dextrin present is precipitated with alcohol and carries the oil down with it, leaving a clear supernatant aqueous-alcoholic layer. Kaolin is added to obtain a powdery precipitate which, after filtration, can be washed free from oil with ether.

Weigh 5 to 10 g. of extract in a beaker and mix thoroughly with distilled water, using 3 ml. for every g. taken. Add alcohol, in the ratio of 8 parts of absolute alcohol to 5 parts of the above dilution, and 0·4 g. of purified kaolin. Stir thoroughly and allow the precipitate to settle. Filter the clear supernatant liquid through filter-paper of ordinary grade, and add to the precipitate about 50 ml. of 70 per cent. alcohol, stir again, and allow the precipitate to settle. Filter and collect the residue in the filter, washing out the beaker with 70 per cent. alcohol. When the precipitate has been drained, wash the residue with ether from a wash-bottle and collect the ether in a separating funnel. Any precipitate adhering to the paper should be separated with a rounded glass rod. Continue washing with ether until a drop of the washings shows no film of oil on evaporation; about 150 ml. are necessary. Wash the ether in the separating funnel with three portions of 30 ml. each of water. Evaporate, add a few ml. of absolute alcohol, re-evaporate, cool and weigh the residue.

In practice it has been found advisable to use an 11-cm. filter-paper and to wash the residue with a little strong alcohol before the ether. Extraction of the oil is usually almost complete after about 100 ml. of ether have been used, but in this method of washing complete extraction is difficult.

A modification of this process is extraction of the oil by placing the wet filter-paper and contents in a Soxhlet thimble and extracting as usual with ether for two or three hours, and then transferring the extract to a separator and washing with water as directed above. Considerably less ether is used and complete extraction is more certain. In all experiments during this work, both for oil determination and vitamin A content, the filter-papers used for extraction with cold ether were submitted afterwards to this Soxhlet extraction. Figures are given later.

Applications of modifications to reduce the filtration period were not successful. Rapid filter-papers allowed finely-divided solid matter to pass through, and suction-filters and Gooch pads became clogged.

It is necessary to evaporate and dry all extracted oils in an atmosphere of nitrogen, not only for vitamin A determination, but also for oil assay. It is to be expected that a highly unsaturated oil, such as cod-liver oil, would easily gain in weight if heated in air, and the following results confirm the necessity for caution in drying oil that has been extracted from a mixture with extract of malt.

A solvent was prepared by shaking equal parts of ether and light petroleum with one-fifth its volume of water plus one-tenth volume of alcohol and 1/50th volume of ammonia solution (sp.gr. 0·880) and separating the solvent layer. Oil was dissolved in it so that it contained 0·2513 g. in each 25-ml. portion, *i.e.* approximately the amount weighed in the Rose–Gottlieb method.

(*a*) Twenty-five ml. were evaporated in a wide-necked extraction flask, the residue was re-evaporated with a few ml. of acetone and the final residue was heated for twenty minutes at 100° C. Weight of oil, 0·2551 g.

(*b*) Oil from (*a*) was heated for a further twenty minutes at 100° C. Weight of oil, 0·2568 g.

(*c*) Twenty-five ml. were evaporated and dried as in (*a*), but with the use of a Brewis flask, *i.e.* with a large surface exposed. Weight of oil, 0·2881 g.

(*d*) Twenty-five ml. were evaporated and dried with acetone in an atmosphere of nitrogen, the flask being partly immersed in hot water. Weight of oil, 0·2508 g.

Further experiments on similar lines with quantities of oil approximating to the amount weighed in the Gunn and Venables method gave comparable results.

(*e*) 0·9039 g., dried for twenty minutes at 100° C., weighed 0·9090 g.

(*f*) Oil from (*e*) heated for a further twenty minutes at 100° C. weighed 0·9118 g.

(*g*) 0·8212 g., dried, as in (*d*), in nitrogen, weighed 0·8214 g.

To test the accuracy of the two methods advocated, fresh cod-liver oil was stirred with approximately ten times its weight of malt extract in a small beaker until emulsified, and the whole was then assayed, with the results shown in Table II.

Extract of malt will give 1 or 2 mg. of residue in these determinations.

It is realised that the experiments described above are not strictly comparable with estimations on commercial preparations, since the degree of emulsification was probably less and other substances are often introduced by manufacturers into the preparation; different brands of extract of malt with cod-liver oil may vary considerably in their power of emulsifying extracting solvents.

The official Extract of Malt with Cod-liver Oil containing 10 per cent. of oil is formulated on a weight in weight basis, and is stated to contain approximately 15 per cent. v/v of oil. Large batches are most conveniently manufactured by volume measure, and this is the common practice. For investigation of the oil-content it was thought preferable to examine samples from material prepared by weight. A representative working batch of about three tons was manufactured for us entirely by weight and contained 10·64 per cent. of oil w/w; by calculation of the sp.gr. of the malt extract from its refractive index—a result which must be accepted with some reserve—the percentage of oil in the finished product was 15·53 per cent. v/v. At intervals throughout the running of the batch six samples of the mixture were drawn into containers. Samples of the original oil and the malt extract used were also obtained. The samples were kept under what was considered average storage conditions, in the dark brown screw-capped bottles generally used for this preparation, on a laboratory bench in a well-lighted room but not in direct sunlight. Sample No. 1 was examined immediately on delivery, and samples 2 to 6 were opened successively at monthly intervals. The following results were obtained:—

TABLE II

Method	Malt used g.	Oil weighed g.	Oil recovered g.
Modified Gunn and Venables	6·599	0·664	0·665
Rose–Gottlieb (centrifuged)	4·540	0·523	0·515
,, ,, ,,	2·349	0·313	0·315
,, ,, ,,	0·934	0·098	0·099

TABLE III

PERCENTAGE OF OIL FOUND

Method	No. 1	No. 2 1 month	No. 3 2 months	No. 4 3 months	No. 5 4 months	No. 6 5 months
Gunn and Venables	10·53 (0·37)	10·59 (0·15)	10·31 (0·08) 10·36 (0·13) 10·33 (0·11)	10·23 (0·41)	10·07 (0·14)	9·96 (0·12)
Gunn and Venables, modified ..	10·73	10·45	10·24 10·28	10·28	10·07	9·85
Gunn and Venables, ether not washed	10·78	10·67	10·44	—	—	10·03
Average ..	10·71	10·58	10·33	10·26	10·07	9·95
Rose–Gottlieb, heated, not centrifuged ..	10·77	10·56 10·53	10·24 10·39	10·21	10·17	10·47
Rose–Gottlieb, centrifuged ..	—	10·51	10·57 10·62 10·51	—	—	—
Rose–Gottlieb, not heated, centrifuged	10·77	10·47	10·30	10·27	10·15	10·41 10·34
Average ..	10·77	10·51	10·44	10·24	10·16	10·41

Extract of malt (by Gunn and Venables method) 0·04
,, ,, (by Rose–Gottlieb method) 0·05

It is to be noted that extract of malt yields a small quantity of ether-soluble material. The figures in brackets in Table III are additional oil found by Soxhlet extraction and included in the totals.

The results were not considered satisfactory, since non-uniformity throughout the mass would not account for such large differences; manufacturers consider a very small figure as likely for maximum deviation in oil-content of different parts of the batch. Further, an unusual discrepancy was observed between the results obtained by different methods in sample No. 6; this was evident also, but to a much less extent, in No. 5.

The possibility that the ether and light petroleum in the Rose–Gottlieb method needed washing with water before evaporation was investigated. Washing is not necessary, but unexpected results were obtained.

TABLE IV

ROSE–GOTTLIEB METHOD

Sample		Ethers washed Oil Per Cent.	Ethers not washed Oil Per Cent.	Original content (Table III) Oil Per Cent.
No. 2	..	10·71	10·75	10·51
No. 4	..	10·71	10·81	10·24
No. 6	..	10·92	10·80	10·41

It will be seen that a considerable increase in apparent oil-content, evidently due to increase in the weight of oil by oxidation, had occurred; the time of determination was one year after the investigation was begun. Conversely, the Gunn and Venables method gave a considerable decrease in apparent oil-content with age; this will be discussed later, but the reason for the discrepancies in the later specimens in Table III becomes more apparent.

After a further six months (18 months from the beginning of the investigation) the samples were re-tested (Table V).

TABLE V

ROSE–GOTTLIEB METHOD

Samples tested 18 months after the beginning of the investigation

Sample		Amount taken approx. 1 g. Oil Per Cent.	Amount taken approx. 2·5 g. Oil Per Cent.	Original content (Table III) Oil Per Cent.
No. 1	..	10·88	10·90	10·77
No. 2	..	10·76	10·90	10·51
No. 3	..	10·85	10·88	10·44
No. 4	..	11·29	11·16*	10·24
No. 5	..	10·81	10·92	10·16
No. 6	..	11·00	11·03	10·41

* The extracted oil, 0·286 g., with 3 g. of extract of malt gave by the Gunn and Venables method 0·231 g. of oil = 9·01 per cent. calculated on the original weight taken for the Rose–Gottlieb method.

The results are a little higher than in Table IV and rather discordant. The alkaline residues, after acidification, gave small, variable yields of fatty acids; partition of strongly hydrolysed soap might explain such variance.

The effect of the age of the samples on the results obtained by the Gunn and Venables method is more remarkable (Table VI).

TABLE VI

GUNN AND VENABLES METHOD

Samples re-tested several months after the beginning of the investigation

Sample		Oil Per Cent.
No. 1	After 18 months	8·72
		8·83
No. 2	,, 18 ,,	8·95
		8·98
No. 3	,, 18 ,,	8·82
No. 4	,, 18 ,,	9·21
No. 5	,, 18 ,,	8·91
No. 6	,, 6 ,,	9·95*
	,, 12 ,,	9·15
	,, 18 ,,	9·01

* *i.e.* 1 month after opening.

The filtrates from the determination of oil in sample No. 4, after adjustment to 30 per cent. alcoholic strength, yielded a further 2·21 per cent. of semi-liquid oil on extraction with ether, and sample No. 5 similarly gave 2·29 per cent.; the acid value of this extract was 173·7 and the iodine value 130·9.

Hence, as the age of the oil increases, results are lowered in the Gunn and Venables method owing to the increased solubility of a portion of the oil in the alcohol. This possibility was forecast by Evers[5] during a discussion on the method when it was presented at the British Pharmaceutical Conference in 1936.

Specimens of commercial preparations known to have been manufactured from different makes of malt extract were purchased, and the oil was determined by the modified Gunn and Venables and Rose–Gottlieb methods, with the results shown in Table VII.

Here, also, with known fresh samples the results obtained by the methods agreed well.

Jones and McLachlan[6] found a variation of 2·5 to 19·8 per cent. of oil in commercial samples tested by them.

II. DETERMINATION OF VITAMIN A IN EXTRACT OF MALT WITH COD-LIVER OIL.—This investigation was undertaken not only to determine the extent of recovery of vitamin A from the preparation, but also to see whether any idea of the deterioration of the vitamin-content on storage could be gauged.

Jones and Evers[7] examined the oils obtained from commercial preparations of extract of malt with cod-liver oil for vitamin A by the Carr–Price colour test, and by this method observed considerable variation in quality. No literature on the examination of this preparation for recovery of vitamin has been noted.

For quantitative determination of its vitamin A content the oil should be extracted completely. It has been shown that on fresh preparations complete extraction is probably achieved by the Gunn and Venables and Rose–Gottlieb methods; the problem remaining is to find the most suitable modification of these methods that will give the nearest figure to the true vitamin A content.

TABLE VII

	Rose–Gottlieb method Oil Per Cent.	Gunn and Venables method (modified) Oil Per Cent.
A	17·31	17·20
B	10·35	10·01
C	10·50	7·12
After 3 months ..	—	6·43
„ 5 „ ..	—	5·98
D (Halibut oil) ..	5·48	5·33
E*	10·88	10·90
On 5 g.	10·79	—
F*	11·06	11·04
On 5 g.	11·05	—

* Examined within 1 week of manufacture.

The small quantities of oil extracted (0·5 to 0·8 g.) require protection against oxidation. When the oil was extracted by either of the proposed methods without precautions against oxidation the vitamin A content found was low. It was considered advisable to avoid the greatest chance of deterioration, *i.e.* in the drying and weighing of the oil, by making the extraction in duplicate, on the assumption that the percentage extracted and weighed would, by simple calculation, give the equivalent of oil in the vitamin determination. Results showed this method to be quite satisfactory.

The following precautions were considered necessary to obtain full recovery in the assay for vitamin A:

(*a*) Delay was avoided in dissolving, precipitating and filtering in the Gunn and Venables method; when ethereal solutions had to stand between extractions in the Rose–Gottlieb method (*i.e.* when not centrifuged) they were kept under nitrogen.

(*b*) All ethereal solutions of oil were evaporated and cooled under nitrogen.

(*c*) The residual oil was not dried but immediately saponified with alcoholic potash for a maximum of five minutes.

(*d*) The unsaponifiable matter was extracted by the method given in the B.P. Addendum 1936, p. 89.

(*e*) The solution of unsaponifiable matter was evaporated under nitrogen, a few ml. of acetone of analytical reagent quality were added, the liquid was re-evaporated and the unsaponifiable matter was cooled in nitrogen.

(*f*) Spectroscopically pure cyclohexane was introduced into the flask, and the unsaponifiable matter was dissolved before stopping the flow of inert gas. The solution was then diluted to a suitable volume.

(*g*) No delay was allowed before the spectrographic determination; all determinations were completed the same day that they were begun. Absorption spectra were measured by means of a Bellingham and Stanley Medium Quartz Spectrograph with a B-S rotating sector photometer, tungsten-steel electrodes and a high-voltage spark being used.

(*h*) Importance was attached to the purity of the extracting solvents. The ether and light petroleum (b.p. 40°–60° C.) used were of analytical reagent quality.

Direct extraction of the unsaponifiable matter with cyclohexane gave consistent but low results; measurement of absorption by direct transference of the ethereal solution of the unsaponifiable matter to the cell of the spectrophotometer gave very discordant figures.

TABLE VIII

$E^{1\%}_{1cm.}$ $328m\mu$ VALUE OF EXTRACTED OIL

Method		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Gunn and Venables							
(*a*) Modified	No precautions	0·48	—	—	—	—	—
	Weighed: N_2 used	0·51	—	—	—	—	—
	All precautions	0·49	0·52	0·43	0·55	—	—
		0·52	—	0·56	—	—	—
(*b*) Cold extraction	,, ,,	0·56	0·49	0·58	0·49	0·59	0·57
		0·52	0·57	—	0·58	—	—
Rose–Gottlieb							
(*a*) Preliminary heating:	No precautions	0·51	—	—	—	—	—
	All ,,	0·56	0·54	0·58	0·60	—	—
		0·52	—	—	—	—	—
Centrifuged	,, ,,	0·59	0·57	0·55	0·67	—	—
		0·55	—	—	—	—	—
(*b*) No preliminary heating:	,, ,,	0·59	0·60	0·58	0·68	—	—
Centrifuged	,, ,,	0·59	0·62	0·59	0·67	0·58	0·52
		—	—	0·63	—	—	—
Cod-liver oil							
	All precautions	0·60	0·62	0·63	0·65	0·54	0·51
		0·60	—	—	0·64	0·53	—
		0·60	—	—	—	—	—

After the determinations by the original Gunn and Venables method, the residual solid matter was extracted further with ether in a Soxhlet apparatus for two to three hours, and the weight of oil obtained was subtracted from that calculated to be present, before calculating the $E^{1\%}_{1cm.}$ $328m\mu$ value.

From the figures given it will be seen that the Gunn and Venables method yielded slightly low divergent results. This was probably due to exposure of the oil in a finely divided state on kaolin during filtration and, in the modified method, to oxidation during three hours' warm extraction. Slight adsorption of vitamin A by the kaolin is possible. Using the Carr–Price colour test, Gunn and Venables found no diminution in vitamin A content in the extracted oils they examined.

The effect of apparently small details is shown in the results for the Rose–Gottlieb method. Consistently lower figures were given when the dilution of extract of malt with cod-liver oil was heated before extraction; this was only for a few minutes, but loss undoubtedly occurs. Centrifuging is of great value in preventing losses on standing between extractions.

Full recovery of vitamin A can be obtained by the Rose–Gottlieb method.

It will be noted that the $E^{1\%}_{1cm.}$ $328m\mu$ value of the original oil and of the oil contained in the malt extract rises to a maximum on keeping. This is in accordance with the observations of previous workers (Griffiths, Hilditch and Rae,[8] Garratt[9]). The investigation was started in November, and it may be noticed that the rapid fall in the $E^{1\%}_{1cm.}$ $328m\mu$ value coincided with longer daylight and rise in average temperatures. It should also be borne in mind that the bottle of cod-liver oil used as a standard for comparison was opened repeatedly during the investigation.

After use the samples were closed and kept under similar conditions and re-tested after further periods in order to observe any deterioration. The following results were obtained:

TABLE IX

Sample		Time after original opening	$E^{1\%}_{1\,cm}$ $328m\mu$	Time after original opening	$E^{1\%}_{1cm.}$ $328m\mu$
No. 1	..	4 months	0·52	7 months	0·47
				12 ,,	0·49
No. 2	..	3 ,,	0·55	6 ,,	0·46
No. 3	..	2 ,,	0·54	5 ,,	0·48
No. 4	..	1 month	0·53	4 ,,	0·45
No. 5	..	..	—	3 ,,	0·42
No. 6	..	..	—	2 ,,	0·44
Cod-liver oil			0·43		0·44

The shape of the absorption curve of the cod-liver oil, after twelve months' standing, was normal, with a slight shift further into the ultra-violet; the absorption curve for the oil extracted after twelve months from the malt extract with cod-liver oil showed practically no inflexion and a decided shift into the ultra-violet. It has been found (Robinson,[10] Smith[11]) that oxidation products of vitamin A may show considerable absorption at $328m\mu$ and, as the band showed poor persistence, the figure for $E^{1\%}_{1cm.}$ $328m\mu$ of the vitamin A in Sample No. 1 thus obtained by spectrophotometric assay after 12 months is probably in excess of the corresponding true vitamin A content.

These experiments indicate that under normal storage conditions little loss of vitamin A occurs in extract of malt with cod-liver oil within six months of manufacture, and the deterioration was even less than that of the original oil under the same conditions (although, as stated above, the latter was opened more frequently). After 12 months, deterioration had progressed, and the samples which had been opened frequently then had an unpleasant taste and odour and had darkened considerably.

SUMMARY.—Various methods for the determination of oil in Extract of Malt with Cod-liver Oil have been considered with a view to accurate determination both of the oil and the vitamin A content. The Rose–Gottlieb and Gunn and Venables methods were considered most suitable to satisfy both requirements and have been critically compared. For fresh preparations both methods gave results that agreed well and afforded an accurate measure of the oil-content, but with increase in age of the preparation the Gunn and Venables method gave low results.

The vitamin A content of the extracted oil has been determined spectrophotometrically; it has been shown that full recovery could be obtained when the Rose–Gottlieb method of extraction of the oil was used, provided that precautions were taken against oxidation. Slightly lower figures were found by the Gunn and Venables method.

In view of the findings summarised above, the method recommended for the determination of oil in Extract of Malt with Cod-liver Oil and of vitamin A in the extracted oil, is the Rose–Gottlieb method, modified by use of a centrifuge and with precautions taken against oxidation.

Duplicate extraction is advocated—one for assay of oil-content, the other for vitamin A determination. Little loss of vitamin A occurs in Extract of Malt with Cod-liver Oil for some months under normal conditions of storage.

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DISCUSSION

Mr. N. EVERS congratulated Dr. Garratt on this thorough piece of work. He, himself, had had some experience of trying to determine the oil in malt extract and oil and, until recently, had not been successful. He had used the Rose–Gottlieb method before the Gunn and Venables method was published and had found it quite satisfactory. He had been able to test Dr. Garratt's modification of the Gunn and Venables method and, on the whole, he did not quite agree with Dr. Garratt that the Gunn and Venables method gave lower results than the Rose–Gottlieb method—he had found that it gave slightly higher results. It also had the advantage of enabling one to use a larger quantity of the sample. He was surprised that this oxidation of the oils, and also the development of acidity, occurred in these emulsions. One would expect that the oil would be protected against oxidation in a fine emulsion of this kind. He asked if Dr. Garratt had tried to determine the vitamin A not recovered in the oil extracts.

Mr. PINDER mentioned that Dr. Garratt had suggested that one of the possibilities might be due to the length of time the precipitate had to drain on the filter-paper. He, himself, had tried to adapt the Gunn and Venables method to the determination of fat in milk. He had found that the inner tube of a Bolton and Williams extractor could be fitted by means of a bung to a Buchner filter-flask, and, if the cotton wool at the bottom of the extractor tube was carefully packed and a moderate vacuum was used, the precipitate could be filtered off and washed in a very short time. The bung was then removed and the tube placed in the extractor and extracted in the usual way. Some such technique might possibly be developed to enable the oil to be rapidly extracted from an admixture with extract of malt.

Mr. NICHOLLS observed that he had tried this method of getting a measure of the vitamin A by extracting a portion of the oil and had obtained high results. It was fairly obvious that one did not get the same distribution of the total oil and vitamin A between the upper and the lower layers.

Mr. S. G. STEVENS suggested that possibly the slightly increased weight might be due to the flavouring that was sometimes added. He would also like to know what standard Dr. Garratt proposed for a B.P. extract.

Dr. GARRATT, replying, remarked that he was quite prepared to hear criticisms to the effect that with the Gunn and Venables method better vitamin recovery might be obtained by some workers than by others; it was a question of the personal interpretation of the technique of the method and that the small details involved might have a pronounced effect on the estimation of vitamin A. He thought that Mr. Evers would agree that the discrepancy was very small and would not lead to the rejection of a sample. He had not attempted the recovery of vitamin A from the fatty extracts. The question of flavouring had not come into the investigation, as he knew from the manufacturers what flavouring had been used; the proportion was small, and the non-volatile matter in it was within the experimental error of the determination. If flavouring were added in any quantity, the analyst must do his best to separate it. He had tried Mr. Pinder's suggested method of extraction of malt and oil and found that it clogged the filters. He understood that standards for malt and cod-liver oil were being prepared.

Tests available for the Identification of small quantities of the War Gases

By H. E. COX, D.Sc., Ph.D., F.I.C.

It appears that the Public Analyst may at any time be called upon to test suspected foodstuffs for contamination with the war gases. Such work will have to be done promptly, so it is desirable to be prepared for it by having the necessary materials and tests ready to hand. In a recent paper in *Chemistry and Industry*,[18] A. P. B. Page has described the principles which operate in relation to the absorption, contamination and de-contamination of foodstuffs by poisonous gases and vapours, but he does not give details of any practical tests. The Home Office A.R.P. Department have issued a Memorandum No. C.9 "On the detection and identification of War Gases."* This consists primarily of notes for the use of gas Identification Officers who may not normally have opportunity for carrying out chemical work on the identification of war gases. It includes, however, a résumé of the methods available for the chemical identification of the more important gases and of laboratory technique employed in the handling of contaminated materials, but it does not give analytical details applicable to small quantities. The Memorandum expresses the opinion that, in general, air-flow analysis will be the simplest and most satisfactory method for the examination of contaminated materials. It would not usually be difficult to devise a simple bubbler through which to aspirate air slowly after passing it round or through the suspect material, which may with advantage be warmed to volatilise more readily any liquid "gases." So far as possible, rubber joints should be excluded, and the use of small sintered-glass diffusers will enable the gas to be passed into, and absorbed by, a minimum volume of the reagents employed for the tests. The number of gases which undergo hydrolysis in water or dilute alkali indicates that in many cases it will be possible to make direct tests for the products of hydrolysis in the aqueous portion of materials which contain much water. Contamination with arsenical dusts as a group will be readily detected by a determination of arsenic by the well-known methods of wet oxidation, which may be applied to the foodstuff itself.

For the examination of some materials, not foods, J. Studinger[5] suggests extraction with a dry organic solvent. This may sometimes be a convenient procedure, as it has the advantage that all the war gases are soluble in organic solvents. When a solvent is employed, anhydrous ether or benzene is to be preferred, not one containing a halogen.

Although it seems that the gases most likely to be encountered are mustard gas and the organic arsenicals such as Lewisite or the arsenical dusts, mixtures may occur. Hence, it is necessary to be prepared to identify a wider variety of poisonous gases, and, with this in view, the following notes have been put together. The tests or reactions are mostly well known, and have been collected from various sources, those that are applicable to minimal quantities being particularly selected. When larger quantities are available, identification by means of the usual physical

* H.M. Stationery Office, York House, Kingsway, W.C. Price 1s. 3d.

constants and major chemical reactions, such as are described by Sartori in his recent book,[1] should be fairly simple. It is hoped that the following notes will be of service should the necessity for such examinations unfortunately arise.

(1) CHLORINE (Cl).—The tests for this element are too well known to need any repetition, but it should be noted that impure phosgene or diphosgene gives most of the reactions of chlorine in solution, such as the *o*-tolidine reaction and the blue colour with aniline acetate paper.

Details for the preparation of a sensitive *o*-tolidine paper are given in a D.S.I.R. Leaflet (No. 10) on the Detection of Toxic Gases in Industry.[2] Another very sensitive test available for chlorine or bromine vapour in air is due to Eichler.[3] Resorufin in alkaline solution has an intense fluorescence which is changed or destroyed by halogens. A drop of a reagent consisting of 0·1 g. of resorufin and 1·5 g. of sodium carbonate in 100 ml. of water is added to 5 ml. of water, and the suspect air is passed through it. A blue colour (resorcin blue) is produced by chlorine or bromine, or, if the halogen is in excess, both the colour and the fluorescence are destroyed.

(2) PHOSGENE ($COCl_2$) is soluble in water and rapidly hydrolysed therein to hydrochloric acid, and so gives the usual colour with indicators such as methyl orange. Passed into a 1 per cent. solution of potassium iodide containing starch, a blue colour results. Traces of phosgene may be determined by bubbling a known volume of the air through 10 ml. of solution containing 1 ml. of 0·1 N sodium hydroxide solution and 5 ml. of alcohol. The liquid is then evaporated on the water-bath to 2 ml., acidified with acetic acid and evaporated to dryness, the residue is moistened and re-evaporated, and the chloride is titrated with $N/40$ silver nitrate.[4]

If chlorine is also present it may be removed at the outset by passing the gas through cotton-wool previously soaked with potassium iodide solution and dried. J. Studinger[5] and Kretov[6] quote the following test as specific for phosgene:

A filter-paper is soaked in a mixture of 5 ml. of a 0·5 per cent. solution of 1:3:6-nitroso-dimethyl-aminophenol and 2 ml. of a 0·5 per cent. solution of *m*-diethyl-aminophenol, both in xylene; this paper gives a green colour with traces of phosgene. If the paper has become dry it should be moistened with alcohol before use. Phosgene forms diphenylurea (m.p. 235° C.) when passed into an aqueous solution of aniline (Kling and Schmutz[7]). The reaction is sensitive and may be applied by bubbling the suspect air through about 3 ml. of a saturated aqueous solution of aniline; a white turbidity forms and then a crystalline precipitate, which may be collected and dried at 70° C.

A very sensitive drop reaction is described by Anger and Wang.[8] A granule of phenylhydrazine cinnamate is added to a drop of the solution of the suspect substance in chloroform or carbon tetrachloride and followed, after five minutes, by a drop of 1 per cent. copper sulphate solution; a red-violet colour of the diphenyl carbazide is produced in presence of phosgene. As little as 0·5γ can be detected. The test can also be applied by means of filter-paper impregnated with copper sulphate, dried, and dusted with the phenylhydrazine cinnamate; in presence of a drop of water phosgene produces the violet colour if the concentration is as little as 1:50,000.

(3) DIPHOSGENE ($COCl.OCCl_3$) reacts only feebly with cold water, but with hot water forms hydrochloric acid. It is decomposed on heating, or on contact with a porous material, into two molecules of phosgene. When the gas is passed into excess of sodium phenate solution a white precipitate of diphenylcarbonate, insoluble in cold water, m.p. 110–111° C., is formed. If the suspect gas is passed through a tube heated at 300–350° C. it is completely decomposed into phosgene and gives the reactions shown above (2).

(4) METHYL CHLOROFORMATE ($ClCOOCH_3$) is a volatile liquid boiling at 71° C.; it is not decomposed by cold water, but is hydrolysed by hot water or by alkali, with the production of methyl alcohol and hydrochloric acid; whereas the chloro-methyl chloroformates all produce chlorine as well as hydrochloric acid on hydrolysis, and therefore liberate iodine from potassium iodide. It may also be recognised by passing it into an alcoholic solution of aniline; hydrochloric acid is then produced. It does not liberate iodine from potassium iodide.

(5) CHLOROPICRIN ($CCl_3.NO_2$), known as PS., has a characteristic sweet smell; its vapour is insoluble in water and is not decomposed by it. Filter-paper impregnated with a petroleum spirit solution of Sudan red is turned a blood-red colour by it. On being passed through a tube heated to about 450° C. it is decomposed, and chlorine may be detected in the usual way; it gives the Beilstein halogen test quite easily. When chloropicrin is passed into an alcoholic solution of potassium iodide, potassium nitrite and potassium chloride are formed, and the former may be detected by the well-known Griess–Ilosvay reaction; the finding of nitrite is practically definitive of chloropicrin. Passed into 2 ml. of hot alcoholic potassium hydroxide solution containing a drop of aniline the characteristic smell of carbylamine appears. If a sufficient quantity is available the following test is useful:—A drop of the liquid is boiled with a 5 per cent. alcoholic potassium hydroxide solution, or the suspect air is bubbled through the hot solution and a few crystals of resorcinol are added; a red colour, due to the nitroso compound, is then obtained on the addition of sulphuric acid (Guillemard and Labat[9]).

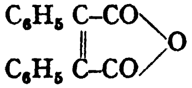
(6) BENZYL BROMIDE ($C_6H_5.CH_2Br$) AND XYLYL BROMIDE ($CH_3.C_6H_4.CH_2Br$).—These two gases are similar; they are only slowly decomposed by water, but are readily hydrolysed by alkali. When they are passed into an alcoholic solution of silver acetate a precipitate of silver bromide is immediately produced. When they are passed into a hot alkaline solution of potassium permanganate, benzoic or one of the phthalic acids, respectively, is formed. The acid may be isolated by acidifying and extracting with ether, and identified by the usual tests. Phthalic acid is quickly detected by heating the residue for a few minutes to 160° C. with resorcinol and conc. sulphuric acid; after cooling, an excess of sodium hydroxide produces fluorescein. Benzoic acid gives Mohler's reaction.

(7) BROMOACETONE (B.A.) ($CH_3.CO.CH_2Br$) AND BROMOMETHYLETHYLKETONE ($C_2H_5.CO.CH_2Br$ and $CH_3CO.CHBrCH_3$) are similar in properties; they are slightly soluble in water and are not decomposed thereby. The vapour is quickly absorbed in warm 0·5 *N* alcoholic potassium hydroxide solution, forming potassium bromide and the hydroxy ketone. The ketone may be identified by the addition of a few drops of sodium nitroprusside solution to a solution of the gas in the alkaline hydroxide; acetone gives a red, and methyl-ethyl-ketone an

orange colour; the acetone colour is intensified on the addition of acetic acid. Another method is to pass the gas into sodium hydroxide solution, then add a few drops of an alcoholic solution of *o*-nitro-benzaldehyde, which combines with acetone to form indigo, or with methyl-ethyl-ketone to produce a brown colour. This test is not quite so sensitive as the nitroprusside reaction. If sufficient material is available, it may be combined with 2 : 4-dinitrophenylhydrazine to form the nitro-hydrazone. To 1 ml. of a 1 per cent. alcoholic solution of dinitrophenylhydrazine 1 drop of hydrochloric acid and few drops of the alcoholic solution of the substance are added. The mixture is kept at room temperature until crystals of the nitrophenylhydrazone separate; a few more drops of hydrochloric acid may help the crystallisation. The melting-point of the acetone compound is 148° C., and that of the methyl-ethyl-ketone compound 128° C.

(8) Ethyl Bromoacetate ($CH_2Br.COOC_2H_5$) and (9) Ethyl Iodoacetate (K.S.K.) ($CH_2I.COOC_2H_5$).—These products are slowly decomposed by water, forming bromo- and iodo-acetic acids, respectively. They are quickly absorbed by alcoholic potassium hydroxide solution, forming potassium bromide and iodide, respectively, together with glycollic acid. Glycollic acid is characterised by adding to the alkaline solution a small particle of guaiacol and then a few drops of sulphuric acid on warming, a violet colour is produced. It is pointed out, however, that the finding of iodide after hydrolysis is fairly certain to indicate the presence of K.S.K.

(10) Bromobenzylcyanide (B.B.C.) ($C_6H_5CHBr.CN$).—This compound when pure is a solid, but it may be dissolved or mixed with chloropicrin or other gas. It is not soluble in water, but readily so in organic solvents, and is quickly hydrolysed, even in the cold, by alcoholic potassium hydroxide, with the formation of potassium bromide and dicyanostilbene ($(C_6H_5.C.CN)_2$). This, on boiling, gives off ammonia, and, if the solution is then cooled and acidified, a yellow precipitate of diphenyl maleic anhydride



(m.p. 156° C.) is obtained.

Concentrated sulphuric acid gives a deep red colour on warming with a tiny droplet of bromobenzylcyanide. A non-specific reaction for B.B.C. is the blood-red colour that it gives with Sudan red. A filter-paper lightly coloured by means of a solution of the dye in petroleum spirit gives this blood-red colour.[*] A similar reaction in a more sensitive form can be obtained by passing the gas through a plug of cotton-wool tinted with Sudan red by wetting the wool with the petroleum spirit solution and drying it. It should be noted that bromobenzyl cyanide, being really a nitrile, does not give a cyanide reaction after hydrolysis with alcoholic potash. Benzyl cyanide may, however, be present as an impurity.

(11) Chloroacetophenone (C.A.P.) ($C_6H_5.CO.CH_2Cl$) is soluble in most organic solvents, but is unaffected by water. It is hydrolysed at once by warm alkaline solutions and the chloride can be recognised. The gas passed into alcoholic ammonia forms indole, which can be oxidised to indigo by addition of perhydrol or recognised by the red colour produced on adding *p*-dimethylaminobenzaldehyde solution to the acidified liquid.

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[*] This test is described by Ligtenberg, but I do not find that it works well.—H. E. C.

(12) DIPHENYLCHLOROARSINE (D.A.) ($[C_6H_5]_2$ AsCl) AND (13) DIPHENYLAMINECHLOROARSINE (D.M.) ($[C_6H_4]_2$. NH.AsCl).—Both substances are volatile solids, and are quickly hydrolysed by water, with the formation of hydrochloric acid with diphenylarsenious oxide and diphenylaminearsenious oxide, respectively. Hence they may be recognised by the Gutzeit test after decomposition with nitric acid and sulphuric acid in the usual way. To differentiate the amino-compound, a small quantity of vapour is passed into sulphuric acid, which gives a red colour with the diphenylamine compound, and a blue when a trace of nitrate is added. Both compounds may be distinguished from the corresponding cyanides by the absence of hydrogen cyanide in the products of hydrolysis. A shorter test for the arsenic is to pass the vapour into an acidified solution of potassium permanganate, which is decolorised; arsenic is then easily identified in the solution.

(14) DIPHENYLCYANARSINE (D.C.) ($[C_6H_5]_2$. AsCN) AND (15) DIPHENYLAMINECYANARSINE ($[C_6H_4]_2$.NH.AsCN).—Both compounds are only slowly affected by water, but are quickly hydrolysed by alcoholic potassium hydroxide, with formation of the corresponding phenyl or phenylamine arsenious oxide and potassium cyanide. Both absorb iodine quantitatively from alcoholic iodine solution. The cyanide produced on hydrolysis is recognisable by acidifying the alkaline solution and warming it while a piece of filter-paper, previously soaked in a mixture of benzidine and copper acetates, is held in the tube.* A blue colour is produced by cyanide. The Prussian blue reaction, obtained by adding a crystal of ferrous sulphate and a drop of ferric chloride solution, and then boiling and acidifying with hydrochloric acid, is more specific and very sensitive. Both compounds reduce an alkaline solution of potassium permanganate, and the arsenic can then be detected as usual by the Gutzeit test.

(16) DICHLORODIETHYL SULPHIDE (MUSTARD GAS) ($[CH_2.CH_2.Cl]_2S$).—This compound is hydrolysed in water to produce hydrochloric acid and thiodiglycol, so that a first indication is the colour change of an indicator such as methyl red. Studinger (*loc. cit.*)[5] describes several of the large number of tests which have been published for this gas. The following are specific:

A 0·1 per cent. solution of gold chloride is dried on filter-paper; a deep yellow spot or stain is produced on it by mustard gas. Grignard's test: 20 g. of sodium iodide, 40 drops of a 7·5 per cent. solution of copper sulphate, and 2 ml. of a 35 per cent. gum arabic solution are dissolved in 200 ml. of water. Air, thought to contain mustard gas, is slowly bubbled through 1 ml. of this reagent, or a drop of solution of the gas is added. A yellow colloidal precipitate of diiodoethyl sulphide is formed in presence of mustard gas. Quite a small quantity of dichlorodiethyl sulphide, when bubbled into 1 ml. of a 20 per cent. aqueous solution of sodium sulphide, quickly gives a precipitate of diethylenesulphide (m.p. 111° C.). When mustard gas is passed into 1 ml. of a freshly prepared alcoholic solution of β-naphthol mixed with an equal volume of 0·1 N sodium hydroxide a turbidity, due to dinaphthylthioether, is produced with as little as 0·06 mg. of the gas. Filter-paper, dipped into a 2 per cent. solution of sodium platinum iodide, is turned first purple, then blue, when exposed to air containing this gas.

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* The method of making a sensitive benzidine copper acetate paper is described in the pamphlet on *Toxic Gases in Industry*, II, issued by H.M. Stationery Office. (*Cf.* ANALYST, 1938, 63, 659.)

(17) CHLOROVINYLARSINE (LEWISITE) ($CHCl:CHAsCl_2$) has an odour of geraniums. It is rapidly hydrolysed by water, producing hydrochloric acid and chlorovinylarsenious oxide. Reactions for acid, chloride and arsenic will therefore be obtained. When Lewisite is passed into 1 ml. of a 15 per cent. solution of sodium hydroxide there are formed acetylene, sodium chloride and sodium arsenite. The acetylene can be recognised by suspending a piece of cuprous chloride paper above the alkali; a red stain is produced by acetylene. The arsenic is shown by a direct Gutzeit test. As by other chloroarsines, a white precipitate of the alkyl arsine sulphide is quickly produced on passing the suspect air or gas through a few ml. of water and then adding 3 drops of hydrogen sulphide water. Excess of hydrogen sulphide must be avoided, and then, according to Nametkin and Nekrassov,[10] the test is sensitive to 0·02 to 0·05 mg.

(18) ETHYLDICHLOROARSINE (DICK) ($C_2H_5AsCl_2$) AND (19) METHYL DICHLOROARSINE (CH_3 $AsCl_2$).—Both compounds are quickly decomposed by water, just as is Lewisite, producing hydrochloric acid and the alkyl arsenious oxide. They both give the sulphide reaction with hydrogen sulphide, as described under Lewisite, but no acetylene is formed on absorption with sodium hydroxide. These two reactions therefore serve to distinguish the ethyl and methyl compounds from the vinyl compound. When these gases are passed into 1 ml. of mercurous nitrate solution just acidified with nitric acid, an immediate grey precipitate of metallic mercury is obtained from methyl dichloroarsine, and a white precipitate, changing slowly to grey, is produced by the ethyl compound.

(20) PHENYLCARBYLAMINE CHLORIDE (C_6H_5. $N.C.Cl_2$) is a slightly volatile oily liquid with an odour of onions; it is not hydrolysed by water and does not produce acid. Passed into hydrogen sulphide water it produces hydrochloric acid and phenylcarbylamine; hence it can be recognised by adding a few drops of hydrogen sulphide water to a benzene solution of the gas or benzene through which the suspect air has been passed. It gives reactions for chloride and phenylcarbylamine on absorption by alcoholic potassium hydroxide. Phenylcarbylamine chloride gives a Grignard reaction resembling that with mustard gas, but may be distinguished from that gas by the absence of acid and sulphur and by the other reactions described above. Ligtenberg[11] gives a test with Sudan red and ferric chloride diluted with chalk.

(21) METHYL (or ETHYL) CHLOROSULPHONATE ($CH_3.SO_3Cl$) is a volatile liquid usually admixed with dimethyl sulphate. It differs from the latter in that in water it is hydrolysed to methyl sulphate and hydrochloric acid. Thus it may be recognised by the liberation of this acid and the formation of potassium sulphate and chloride when aspirated through alcoholic potassium hydroxide solution.

GROUP REACTIONS.—In order to identify these gases most rapidly it may be convenient to apply certain group reactions.

A.—The following gases or vapours give rise to a halogen acid on contact with water, and so may be detected with an indicator, such as methyl red:—Chlorine. Phosgene. Diphosgene. Benzyl or Xylyl bromide (slowly). Diphenylchloroarsine. Diphenylaminechloroarsine (slowly). Methyl and Ethyldichloroarsine. Chlorovinylarsine. Dichlorodiethyl sulphide. Methyl and ethyl chlorosulphonate. Methyl chloro-formate (with hot water).

B.—The following, which do not quickly form an acid with water, are rapidly decomposed by alcoholic potassium hydroxide, giving an alkali halide:—Ethyl bromoacetate. Ethyl iodoacetate. Bromobenzyl cyanide. Bromoacetone. Chloro- and Bromoacetophenone. Phenylcarbylamine chloride. Chloropicrin (reacts only slowly). Diphenylaminechloroarsine.

C.—The following give hydrogen cyanide on hydrolysis with water, and may be detected by the Prussian blue reaction:—Hydrogen cyanide (possibly mixed with stannic salts). Cyanogen chloride (slowly hydrolysed in water, quickly by alkali). Diphenylcyanoarsine. Diphenylaminecyanoarsine.

D.—The following will give an arsenic reaction when absorbed in alkaline permanganate solution:—Diphenylchloroarsine. Diphenylcyanoarsine. Diphenylamine-chloroarsine. Diphenylamine-cyanoarsine. Chlorovinylarsine. Ethyldichloroarsine.

E.—The following will give colours with conc. sulphuric acid:—Diphenylaminechloroarsine (red, cold). Bromobenzylcyanide (red, warm).

Consideration of the known types of gas, such as those dealt with above, indicates that the question of whether or not certain food is poisonous when taken internally will in practice usually resolve itself into the determination of the cyanide or arsenic content, and that for the purpose of assessing the harmfulness or otherwise the quantities might be considered in terms of hydrogen cyanide and arsenious oxide.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SOME FACTORS THAT AFFECT THE ACCURACY OF DETERMINATIONS OF THE THIOCYANOGEN VALUE

THE main object of the experiments described below was to find to what extent variations in the length of time allowed for the interaction of oil and thiocyanogen affect the magnitude of the thiocyanogen value.

Descriptions of determinations based on Kaufmann's method[1,2,3] indicate that the reaction periods employed by different workers differ considerably. In our experiments a series of determinations was made with each oil examined. Different periods of contact of oil and reagent, varying from one hour to twenty-four hours or more, were chosen in such a way as to facilitate the preparation of graphs showing how the thiocyanogen value varies with the reaction period. The method used was essentially that originated by Kaufmann. A series of determinations was also made with reagent solutions prepared with other solvents. These included an acetic acid reagent to which a mixture of definite proportions of pyridine and concentrated sulphuric acid had been added. None of the reagent solutions so prepared offered definite advantages over the simple acetic acid and acetic anhydride mixture of Kaufmann's process and the results obtained are not included in the table.

METHOD.—All apparatus was carefully dried previous to use. Glacial acetic acid and acetic anhydride were mixed in the proportion of 9 volumes to 1 volume and allowed to stand for at least a week. Lead thiocyanate (12·5 g.), which had been well dried over phosphorus pentoxide, was weighed into a brown reagent bottle, 500 ml. of the anhydrous acetic acid were added, and the mixture was kept for as long as possible before use. When the reagent was required 1·5 ml. of pure dry bromine was added, and the mixture was well shaken for an hour and then filtered through two thicknesses of oven-dried filter-paper into a brown bottle. Occasionally a second filtration was necessary. So prepared, the reagent was clear and colourless, or not more than faintly yellow, and about 0·12 *N* in concentration. Quantities of oil of from 0·1 to 0·14 g. were weighed into 250-ml. stoppered flasks. The temperature of the reagent was brought to 20° C., and 20 or 25 ml. were pipetted into the flasks. The proportions of oil and reagent were so adjusted as to provide at least 100 per cent. excess, and in most of the determinations not less than 200 per cent. excess, of thiocyanogen. It was found advisable to have at least 100 per cent., and preferably more than 150 per cent. excess. An excess greater than 200 per cent. did not appear to alter the rate of addition of thiocyanogen or the magnitude of the maximum value obtained. These observations are in agreement with Kaufmann's statements[4] concerning the proportion of reagent that is necessary. Most oils dissolve readily in the acetic solution, but care must be taken to ensure that all the oil dissolves. Carbon tetrachloride was not used in these experiments, but may be incorporated in the reagent. After being allowed to stand in the dark at room temperature for the appropriate time the reaction mixture was poured into 10 ml. of 10 per cent. potassium iodide solution, the reaction flask was well rinsed, first with potassium iodide solution and then with distilled water, and the whole was titrated with 0·05–0·055 *N* thiosulphate solution. It was not always possible to complete the determinations after definite time intervals, but the reaction periods are in terms of whole hours or are stated to the nearest whole hour. "Blanks" were pipetted at about the same time and kept for as nearly as possible the same period under the same conditions as the corresponding reaction mixtures.

Table I shows reaction periods and thiocyanogen values for various types of refined vegetable oils and Table II shows results for fish liver oils. The iodine value (Wijs) of each oil is also given.

TABLE I

THIOCYANOGEN VALUES

Hours	Olive	Olive	Tea-seed	Maize	Maize	Cotton-seed	Soya	Soya	Sesame	Rape	Raw linseed
1	—	—	66·3	71·7	70·2	62·3	73·6	74·2	72·9	71·8	92·4
3	—	—	—	72·8	71·8	62·5	76·3	77·0	73·3	72·2	106·4
5	70·1	72·1	—	71·0	71·9	63·0	77·0	78·0	73·4	—	108·5
6	—	72·3	—	—	—	—	—	—	—	77·0	109·0
7	—	—	69·7	73·2	71·9	—	77·7	79·3	73·5	—	—
9	70·0	—	69·3	73·1	—	—	—	79·6	—	76·0	—
10	—	—	—	—	—	64·4	—	—	—	—	—
13	—	—	70·7	—	—	—	—	—	—	—	—
15	70·9	—	—	74·6	—	64·0	77·8	80·2	74·9	77·6	114·3
16	—	71·2	—	—	72·4	—	—	—	—	—	—
18	—	—	70·4	—	—	—	—	—	—	—	—
20	—	72·1	—	75·0	72·6	64·4	77·0	80·5	75·2	78·5	113·5
22	—	—	—	—	—	—	—	—	—	—	113·6
24	71·0	71·8	—	74·6	72·7	66·1	78·6	81·3	74·9	78·7	112·2
28	71·5	72·5	—	—	—	—	—	—	—	—	—
IODINE VALUES											
1	87·0	85·2	80·6	112·5	110·9	107·7	129·6	132·6	111·3	101·5	180·6

TABLE II

THIOCYANOGEN VALUES

Hours	Cod-liver oil (Medicinal)	Cod-liver oil (Medicinal)	Cod-liver oil (Medicinal)	Shark-liver oil
1	80·8	80·7	—	72·9
3	89·6	—	—	82·8
5	92·5	92·1	91·6	86·2
7	94·4	93·4	96·6	86·7
9	96·5	94·2	—	86·9
13	—	96·4	—	—
15	98·9	97·9	—	89·4
20	98·3	—	98·8	90·9
22	—	98·4	96·9	—
24	99·6	97·9	98·3	88·4
30	—	98·9	—	—
IODINE VALUES				
1	160·7	163·0	167·2	146·4

Though the total number of oils examined was not large enough to justify definite generalisations, useful indications were obtained. From examination of graphs corresponding with the tables above and from the results of other experiments it is evident that olive oil, in which oleic acid constitutes 80 per cent., or more, of the total fatty acids, gives a maximum value (or a value which is nearly a maximum) in about 5 hours. The same is probably true of almond oil and other oils of somewhat similar composition, but for determinations made on these oils and on teaseed oil a 15-hour period is preferable. Examination of vegetable oils which contain little or no linolenic acid but a high proportion of linolic acid relative to the percentage of oleic or other monoethylenic acid indicated that, although a maximum value may occasionally be obtained in 10 hours or even less, it is advisable to allow a contact period of at least 15 hours. Results for the more unsaturated oils were less satisfactory but maximum values were obtained in periods varying from 20 to 24 hours. (Kaufmann[5] allows 24 hours for determinations of thiocyanogen values of fish liver oils.)

In most cases, but especially when dealing with highly unsaturated oils, it was found that results obtained with reaction periods of more than 28 hours are liable to be very inaccurate. Stale reagent or reagent in which there is any precipitate should not be used. In our experience the activity of the reagent is not seriously diminished in 3 days, and good results are obtainable with reagent which is not more than 5 days old. It is, however, much preferable to begin determinations with reagent which is fresh or not more than 2 days old.

H. N. SHER
R. H. COYSH

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3. ——, *Seifensied Ztg.*, 1928, No. 35 Reprint; Abst., ANALYST, 1928, **53**, 613.
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BATTERSEA POLYTECHNIC
LONDON, S.W.11
September 20th, 1939

A RAPID METHOD FOR THE VOLUMETRIC TITRATION OF COPPER IN BRONZE, ETC.

THE following method, though not so accurate as the electrolytic method, gives results sufficiently accurate for rapid routine control analysis. It is so speedy that it forms a suitable check on the electrolytic method when, as sometimes happens, there is not enough time for a duplicate electrolytic assay to be made.

METHOD.—One g. of bronze in drillings, millings or other divided form is weighed into a Philips beaker with a capacity of 800 ml. and dissolved in 10 ml. of a mixture of 250 ml. of strong hydrochloric acid and 50 ml. of strong nitric acid while covered with a watch-glass. The beaker is then kept on the coolest part of the hot-plate until the dense brown fumes have evaporated. The watch-glass and the inside of the beaker are rinsed, 50 ml. of cold water and 7 g. of urea are added, and the mixture is well cooled. A little starch solution and 5 g. of potassium iodide are then added (see Note), and the solution is titrated at once from a 100-ml. burette with thiosulphate solution.

NOTES.—The thiosulphate solution is made with 40 g. of sodium thiosulphate per litre, with about one g. of sodium carbonate per litre.

The 100-ml. burette has a spherical bulb of 50 ml. capacity above a stem consisting of an ordinary 50-ml. burette graduated from 50 to 100 ml.

The thiosulphate solution must be standardised under conditions identical with those in the assays. A convenient amount of copper for such a standard is 0·92 g. of copper of known purity.

It was found that the standardisation and the assay are influenced by the manner in which the potassium iodide is added, either as solid or as 50 per cent. solution. It is essential to titrate the solution as soon as possible after addition of the iodide.

Results.—The following results, taken at random, show the accuracy of the method:

With solid potassium iodide:

$$\left.\begin{array}{lll}1\text{ ml. of thiosulphate} & \equiv & 0\cdot010424\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010428\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010431\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010425\end{array}\right\}\text{ g. of copper}$$

With 50 per cent. potassium iodide solution:

$$\left.\begin{array}{lll}1\text{ ml. of thiosulphate} & \equiv & 0\cdot010438\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010438\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010441\\ \text{,,} \quad \text{,,} & \equiv & 0\cdot010433\end{array}\right\}\text{ g. of copper}$$

BRONZES

Copper taken g.	Tin added g.	Copper found g.
0·9316	0·09	0·9312
0·9256	0·079	0·9260
0·9296	0·06	0·9291
0·9667	0·07	0·9667
0·9570	0·09	0·9576
0·9416	0·057	0·9413
0·9384	0·062	0·9376
0·9542	0·046	0·9540
0·9304	0·07	0·9302

GUN METALS (88/10/2)

Copper taken g.	Tin added g.	Zinc added g.	Copper found g.
0·8827	0·098	0·02	0·8828
0·8885	0·099	0·02	0·8891
0·8916	0·093	0·02	0·8912

In every instance the samples were synthetic alloys. The use of solid iodide appeared to give a sharper end-point.

URSULA F. WILLIS

THE MIDLAND LABORATORY GUILD (1928), LTD.
KING ALFRED'S PLACE
BIRMINGHAM, 1

September, 1939

THE FRENCH OFFICIAL METHOD FOR THE DETERMINATION OF FAT IN FLOURS, PASTRIES AND THE LIKE

In two papers by M. Berlie on the determination of rancidity in flours and semolinas (Abst., ANALYST, 1934, **59**, 629; 1935, **60**, 181) reference is made to the French Official Method for determining fat in flours, breads, edible pastes, etc. This method is described in the *Service de la Répression des Fraudes*, but is not readily accessible in this country. As the method may be of use to analysts who are dealing with problems of rancidity in products of low fat-content, for which the usual methods of extraction are unsuitable, I have made the following translation of it.

FLOURS, BREADS, PASTRIES, EDIBLE PASTES, GROATS AND RASPINGS

Fatty substances.—The determination is made on 5 g. of flour weighed on a small scoop of silver-foil.

Apparatus.—A glass tube of the following dimensions is required: length, 24 cm.; external diameter, 19 mm. One end of the tube is drawn out so as to measure at the extreme tip not more than 6 mm. in diameter. The other end is widened to facilitate the introduction of the sample.

Method.—A small ball of absorbent cotton-wool is placed in the drawn-out pointed end of the tube and lightly compressed by means of a glass rod. The 5-g. sample of flour is carefully introduced, in small quantities at a time, the tube being held vertically and the flour being allowed to fall into it from a height of 1 to 2 cm. The tube is then placed in a stand, an extraction flask, of 60 ml. capacity, is put underneath the drawn-out end, and ether is poured into the upper part of the tube, so as to fill it completely. The flour is allowed to soak up the ether, and as soon as the first drops fall into the flask the tube is corked. The rate of flow of the liquid is regulated by means of the cork, so as to obtain one drop in approximately 10 seconds. When all the ether has passed through the flour the extraction is complete. The drawn-out part of the tube, which always retains a little of the fat, is washed out with ether into the extraction flask. After evaporation of the solvent the flask is placed in an oven at 100° C. for an hour, and then cooled and weighed.

(NOTE.—The heating is omitted when rancidity is to be determined, and the specified solvent (alcohol, 30; ether, 30; chloroform, 40 per cent.) is substituted for ether.)

I have found this method simple to use, and, provided that care is taken, it is rapid and economical.

ENID A. M. BRADFORD

RESEARCH DEPARTMENT,
THE METAL BOX CO., LTD.
WESTFIELDS ROAD
ACTON, W.3
August, 1939

Official Appointments

THE Minister of Health has approved the following appointments:

FRANCIS WILLIAM FREDERICK ARNAUD as Public Analyst for the Borough of Beckenham, as from October 1st, 1939 (September 29th, 1939).

FRANCIS WILLIAM FREDERICK ARNAUD as Public Analyst for the Borough of Chatham, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and JACK HUBERT HAMENCE as Joint Public Analysts for the Borough of Barking, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and JACK HUBERT HAMENCE as Joint Public Analysts for the Borough of Dagenham, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and GEORGE TAYLOR as Joint Public Analysts for the Borough of Leyton, as from October 1st, 1939 (September 29th, 1939).

JOHN WALTER FLINT as Deputy Public Analyst for the County of Kent, as from October 1st, 1939, in addition to F. W. F. Arnaud (September 29th, 1939).

EDWARD HINKS as Public Analyst, and DANIEL DONALD MOIR as Deputy Public Analyst for the Borough of Sutton and Cheam, as from October 1st, 1939 (September 29th, 1939).

WILLIAM LINCOLNE SUTTON as Public Analyst for the Borough of Lowestoft, as from October 1st, 1939 (September 29th, 1939).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

KENT COUNTY COUNCIL

Report of the County Analyst for the Quarter ended June 30th, 1939

Pasteurised Milk.—Fifty-five samples, taken in the streets, were stated by the vendors to be pasteurised, although the milk was not sold as pasteurised or marked as such. Of these 55 milks, 9 had been inefficiently pasteurised.

Lung Mixture.—A mixture sold by a chain stores, was stated to have the same composition as a well-known proprietary mixture, and its composition was disclosed at the time of sale. One of the ingredients that should have been present was Tinctura Camphorae Composita (33 per cent.), but it was entirely lacking. A summons was taken out under the Food and Drugs Act, and the vendors were fined £5 with £3 3s. costs.

Shoddy.—Only 3 of 46 samples contained excessive amounts of water (42·2, 34·0 and 28·0 per cent., respectively). In one instance where a farmer strongly objected to paying for wet shoddy, I advised that he was entitled to compensation in excess of the value of the deficiency of nitrogen. One-third of the shoddies were of rather poor quality and contained less than 6 per cent. of nitrogen. Sometimes a unit of nitrogen in a low grade shoddy costs more than a unit in one of high grade; no doubt this is connected with the railway charges which fall more heavily on the nitrogen unit in poorer shoddies.

House Refuse.—Ground and treated house refuse is always damp and, in addition, contains nearly half its weight of useless mineral matter. I have found that the organic matter seldom exceeds 40 per cent. and much of this is in the form of coke, that is to say, partly burnt household coal. As large quantities of this treated household refuse are now being turned out from various centres its sale is being pushed by various types of advertising. One of the interested firms has undertaken manurial experiments, and the result of these will be known during the autumn. Meanwhile, if this material is purchased at all, it should be purchased in experimental quantities, so that its action on both the plant and the soil can be compared with that of other dressings. It is, of course, a fact that heavy yields of some crops can be obtained on old rubbish tips, but whether the refuse is worth its cost and the charges for carriage, cartage and distribution remains to be seen. However, considerable sums of money have been invested in plant to grind, screen and treat household refuse.

Guano Compound.—This contained 75 per cent. of its nitrogen in the form of sulphate of ammonia. The warranted composition, of course, did not convey to the purchaser the fact that such a large proportion of the fertiliser consisted of sulphate of ammonia. A calculation showed that the value of this compound was about £2 0s. 0d. per ton less than the price paid for it. This is another instance which shows the fallacy of buying this type of compound fertiliser without an enquiry into the amount of guano contained by the compound.

Compound Fish Manure.—This, too, should never be purchased unless a warranty is obtained with respect to its content of fish guano. Samples of compound fish manure examined during the quarter showed that in one instance 90 per cent. of the nitrogen was in the form of sulphate of ammonia. It is highly improbable that the purchaser would have been willing to pay the price asked for this compound had he known more about its actual composition.

WASTE FROM A BUTTON FACTORY.—This waste came from a factory manufacturing buttons from nuts. Analysis showed that, whilst it had not a very high nitrogen-content, it contained upwards of 90 per cent. of organic matter. Unfortunately, both the nitrogen and phosphoric acid contents were low, the former amounting to less than 1 per cent. and the phosphoric acid to 0·2 per cent. For fertilising purposes the waste would be of value to the farmers in the neighbourhood of the works where collection and carting expenses would be low.

COOKED FLAKED WHEAT.—It would seem to be most important that the flaked wheat should be submitted to a considerable amount of heat and this is not always done. Cooked flaked wheat is being fed to farm animals which hitherto have not received wheat as part of their ration, and in these circumstances it is necessary that producers of flaked wheat should take due precautions with regard to the cooking. F. W. F. ARNAUD

CITY OF LEEDS

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1938

LACTOSE IN CHEESE.—A complaint was received from a private purchaser that a sample of cheese contained glass. On examination there were found a large number of small wedge-shaped transparent crystals, composed, not of glass, but of lactose, constituting 1·5 per cent. of the total weight of the cheese. The cheese was a processed one, and no previous record of a similar occurrence can be found in the literature.

CURDS ADULTERATED WITH FLOUR.—A formal sample was found to have been made from skimmed milk and adulterated with 1·8 per cent. of flour.

HYPOPHOSPHITE WINE DEVOID OF HYPOPHOSPHITES.—A medicated wine purporting to contain hypophosphites was found to be devoid of hypophosphite. The sample was a sweet red wine containing 28·5 per cent. of proof spirit and 1·5 per cent. of malt extract. The manufacturer was summoned for giving a false warranty to the retailer and was fined 40s. including costs. C. H. MANLEY

METROPOLITAN BOROUGH OF WOOLWICH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1938

OF the 833 samples of food and drugs examined 506 were purchased informally.

HOT MILK MADE FROM MILK POWDER.—A sample of hot milk taken at a café was found to be a fluid made from machine-skimmed milk powder and water. The sample was deficient in fat to the extent of 93 per cent., and the sp.gr., freezing-point, and proportion of five other constituents were outside the normal range for fresh milk. The figures were as follows:—Fat, 0·21 per cent.; solids-not-fat (including 5·33 per cent. of milk sugar), 10·86 per cent.; proteins, 4·14 per cent.; mineral matter, 0·92 per cent.; citric acid, etc., 0·47 per cent.; sp.gr. at 15·5° C., 1·0415; freezing-point (Hortvet), —0·620° C. The nitric nitrogen (0·0004 per cent.) corresponded with the proportion of nitrates (0·45 per 100,000) in a sample of tap water obtained from the supply at the premises where the "milk" was purchased, thus confirming the amount of tap water added to the milk powder. On being summoned, the defendant admitted the offence and was fined £1 with £1 1s. costs.

CHEESE CONTAINING LACTOSE CRYSTALS.—A sample of bread-and-butter and cheese consisted of five slices of white bread spread with butter and with cheese. A variation in the quantities of ingredients used in the manufacture of the cheese (which was sold, not as cheese, but under a fancy name) led to a complaint that it contained broken glass. Analysis showed that particles, 1/16" to 1/8" long, were present. They were sharp, brittle and tasteless, rhombic prisms, and proved to be crystals of α-lactose hydrate, which had presumably formed gradually as the cheese slowly lost water by evaporation. Correspondence with the manufacturers confirmed the inference that an excessive amount of lactose had been used, and that the water-content had fallen from 55 to 45 per cent. The total lactose-content was 11·1 per cent. expressed as hydrated lactose.

H. AMPHLETT WILLIAMS

Report of the Government Chemist upon the Work of the Government Laboratory

FOR THE YEAR ENDING MARCH 31ST, 1939*

THE chemical work for the various Government Departments has been carried out as before (*cf.* ANALYST, 1938, **63**, 887) at the laboratory at Clement's Inn Passage, Custom House, Geological Survey Museum, Park Royal, and Deptford. The total number of samples examined including those dealt with at the Chemical Stations was 555,045, a decrease of 7504 on the previous year. The chief decreases were in wines, imported beer and samples under the Safeguarding of Industries Act, and increases are noted in samples of tobacco, War Office samples and tea.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter.*—The proportion of water varied from 12 to 16·8 per cent.; 39 samples contained over 16 per cent., 526 between 15 and 16 per cent., 232, 14 to 15 per cent., 39, 13 to 14 per cent., and two, 12 to 13 per cent. The Reichert–Meissl value was under 24 in one sample; 24–26 in 39 samples; 26–28 in 149 samples; 28–30 in 275 samples; 30–32 in 279; 32–34 in 95 samples.

Margarine.—Eight of 127 samples had over 16 per cent. of water.

Cheese.—Water varied from 26·5 to 57·8 per cent.; fat from 9·2 to 39·6 of the cheese, or 19·7 to 59·6 per cent. of the dry matter.

Sheep Dips.—Of the 34 samples examined, only one would not have satisfied the Ministry's requirements when prepared as directed.

Sea Water.—The salinity of 6682 samples of sea water, including 2618 from the Fishery Board for Scotland and 498 taken by the Admiralty, was determined, and the data sent to Copenhagen. In 593 samples the proportion of dissolved oxygen was also determined.

Water and Pollution of Rivers.—To ascertain the condition of fishing streams from the point of view of fish life, 85 samples of river water were examined.

Fertilisers and Feeding Stuffs Act, 1926.—Two fertilisers (compound fertiliser and basic slag) were alleged not to conform with the statutory statements supplied with the articles; a bone meal was alleged to contain an excessive proportion of sand. Eleven feeding stuffs (ground oats, linseed cake, white fish meal, 2 meat and bone meals and 6 feeding meals) were examined. The ground oats contained tapioca starch; the linseed cake contained cyanogenetic glucosides capable of yielding hydrocyanic acid; the white fish meal contained an excess of salt and a deficiency of oil; the six feeding meals were alleged not to conform with the particulars given in the statutory statement. The results obtained confirmed those of the Agricultural Analysts, except that the basic slag and two feeding meals were found to agree with the Statutory Statement within the limits of variation allowed.

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* **Obtainable at H.M. Stationery Office, York House, Kingsway, W.C.2. Price 9d., postage extra.**

Agricultural Produce (Grading and Marking) Act.—National Mark Schemes.—The 265 samples of flour examined included 85 Yeoman flours. Samples of malt extract, and malt extract with cod-liver oil numbered 6; of cider, 137; of perry, 6; of honey, 170. The cheese grades remain as last year, except that the Cream Cheese Regulations, 1938, specify one grade made from cream and containing not less than 60 per cent. of butter-fat on the cheese. Nine hundred and fifty-six samples of cheese were examined, including 266 Cheshire, 64 Stilton, 272 Cheddar, 13 cream, 66 Caerphilly, 209 Lancashire, 55 Wensleydale, 6 Leicester, and 5 Derby cheeses. One hundred and forty-two samples of water from the intakes and water-cress beds were examined.

Land Fertility Committee.—In connection with the scheme for improvement of the soil 139 samples of lime and basic slag were examined.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples examined in connection with duty on beer was 42,293. Of these, 475 were of materials used for brewing. Of 3784 samples taken as a check on declarations of gravity, 46 were found to be under-declared. To check dilution, 692 samples of beer were examined; in 17 samples there was evidence of dilution, and in 5 dilution was equivalent to the addition of over 3 gallons of water per barrel. Of the 15,541 samples of beer examined for drawback, only 46 were found to be over-declared. In the examination for arsenic 29 of 2067 samples contained arsenic slightly in excess of the recommended limit.

Cocoa and Chocolate.—The total number of samples was 12,403. The import samples included 1147 additionally examined for spirit, and coconut oil (liable to Ottawa duty) had to be tested for in 1623 samples.

Dangerous Drugs Act.—Fifty-five samples of suspected goods were examined, and of these, 4 were Indian hemp, and one dried rolls of citrus fruit smeared with traces of opium.

Hydrocarbon Oils Duty.—The standard cone and needle penetration tests remain as before. The total number of samples examined for the presence of hydrocarbon oil was 12,979, of which 5711 were from imported and 7268 from exported goods, and of these 8834 were hydrocarbon oils and the remainder such composite goods as enamels, paints, garage preparations, road dressings, insecticides, printing inks, etc.

Hydrometers and Graduated Vessels.—The accuracy of the various vessels issued to the Customs and Excise Officers was tested, 2506 tests being made. Approximately 1250 Tate saccharometers have now been calibrated and issued.

Safeguarding of Industries Act, 1921.—Listed imported chemicals and substances containing the chemicals are subject to duty, and 6662 such samples were examined.

Silk and Artificial Silk.—Of the total 19,487 samples examined, 7746 were from imported articles concerning which the proportions, if any, of real or artificial silk had to be ascertained; also whether or no the natural gum of silk had been removed from the fibre.

Spirits.—Samples examined included 776 of wood naphtha, other crude methyl alcohol and mineral naphtha; 206 of pyridine and dyes intended for use in the manufacture of methylated spirits (only 4 of the samples were condemned), and 3534 of special denaturants. Gins and liqueurs were tested for strength and character (3313), and of these, 2800 were also tested for sugar and saccharin; 134 samples of 14,448 of exported spirituous preparations were found to be over-declared. The 12,549 samples of imported spirits were mostly sent for determination of their obscuration. Two of 42 samples of imported methyl alcohol were found to be liable to duty owing to potability.* One sample of fusel oil of 21 import samples contained excess ethyl alcohol, as did 5 of 43 samples from British distilleries.

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* Methylic alcohol purified so as to be potable is liable to duty as spirits (Finance Act, 1920).

Sugar, Glucose and Saccharin.—The samples of sugar, including 567 from beet sugar factories, numbered 22,064, and sweetening material 52,891, of which 46,183 were from imported goods. Saccharin was found in many of the 90 samples of imported substances specially examined for its presence, and 529 samples of saccharin and articles containing it were analysed for drawback.

Tea.—Of a total of 14,845 samples of tea examined, 95, representing 269 packages, were reported against, 20 on account of the presence of foreign substances, and 75 as unfit for human consumption. To guard against the presence of adulterants or exhausted leaves, 581 samples of exported tea were examined.

Tobacco.—The number of samples examined during the year again showed a further increase, and reached 207,024 (201,751 in 1938–9). The samples are taken for detection and prevention of adulteration (almost non-existent in this country); for determination of appropriate rate of duty and drawback; to ensure that manufactured tobacco for home consumption complies with the requirements of the tobacco laws; for effective control of denaturing waste tobacco used for agricultural and other purposes.

FOOD AND DRUGS ACTS.—Eight samples of food were examined consisting of milks alleged to be deficient in fat or non-fatty solids, one "appeal to cow" milk, one tea alleged to contain foreign matter, and four jams alleged to be deficient in fruit. All the results were in agreement with those put forward by the prosecution, except that the proportion of foreign matter in the tea was less than alleged, and that one jam could not be stated to be deficient in fruit.

MINISTRY OF HEALTH.—*Condensed Milk.*—Of 128 samples, 10 were reported against; in four the quantity of whole milk to which the contents of the tin were supposed to correspond was over-stated, and in addition 2 samples were deficient in milk-solids or both fat and milk-solids, and 6 samples were wrongly labelled.

Preservatives.—Of 1240 samples of imported dairy produce and 630 of other food substances, including pulped fruit, vegetables in brine, fruit juices, cornflour, etc., 29 were reported against. Of these, 27 contained sulphur dioxide; one sample of liquid egg-yolk contained boric acid, and one of soda fountain preparation contained benzoic acid either contrary to Regulations or in excess of permitted quantities.

OFFICE OF WORKS.—Four samples of water were examined bacteriologically in connection with chlorination of bathing water in the Serpentine and St. James's Park Lake, and 73 samples with a view to securing safe supplies for Government institutions, training camps, etc. D. G. H.

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

CHLORINE

OCCURRENCE.—Dangerous concentrations may be encountered in alkali (electrolytic) works, bleaching works, chemical works, dye-making and dye-using works, tanneries, tinplate works, water purification works, etc.

POISONOUS EFFECTS.—Acute poisoning by chlorine is unusual, as the gas can be recognised by its odour and irritant qualities even in low and harmless concentrations. It can be recognised by smell in as low a concentration as 1 part in 1 million parts of air.

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* Leaflet No. 10. H.M. Stationery Office, July, 1939. Price 3d. net.

The effects of various concentrations in air are as follows:

Parts by vol. (approx.)	Mg. per litre (approx.)	Duration of exposure	Effect
1 in 1000	3·17	Brief exposure	Rapidly fatal—by asphyxia
1 in 10,000	0·32	Few seconds	Intolerable
1 in 20,000	0·16	Thirty minutes	Very dangerous, owing to acute pulmonary oedema
1 in 100,000	0·03	Sixty minutes	Bronchitis
1 in 1,000,000	0·003	Prolonged exposure	Permissible

METHOD OF DETECTION.—A test suitable for industrial use must be capable of detecting at least 1 part of chlorine in 1,000,000 without requiring an inconveniently large sample. The only known test that is sufficiently sensitive depends on the interaction of chlorine and a dilute solution of *o*-tolidine to form a yellow compound, which can be estimated colorimetrically. This method has therefore been adopted as the standard industrial method. The test-papers are approximately one-tenth as sensitive to nitrous fumes as to chlorine.

The test is applied by drawing samples of the air, by means of a hand-pump of definite capacity, through a bubbler containing *o*-tolidine solution until the depth of colour produced is equal to that of one of a series prepared from potassium dichromate solution. From the number of strokes required the concentration is obtained by reference to a table.

Apparatus.—The method of sampling the air, the arrangement of the bubbler, and the type of pump are described and illustrated (*cf.* ANALYST, 1938, 63, 659; 1939, 279).

Preparation of Reagent.—One g. of *o*-tolidine (specially purified—m.p. not lower than 130°–131° C.) is dissolved in 100 ml. of conc. hydrochloric acid (of reagent quality), and the volume is made up to 1 litre with water.

Preparation of Standard Colours.—One g. of potassium dichromate (of reagent quality) is dissolved in 1 litre of water. A series of standards is then made by diluting the following quantities of the 0·1 per cent. solution to 10 ml. in tubes of exactly the same bore as the bubbler.

Standard	Vol. of 0·1 per cent. dichromate solution diluted to 10 ml.
No. 1	5 ml.
„ 2	3 „
„ 3	2 „
„ 4	1 „

If kept in well-sealed bottles in the dark, the standards should not change in six months.

Application of Test.—Ten ml. of the *o*-tolidine solution are measured into the side-arm test-tube of the apparatus, and the tube is connected with the pump, the valves of which have previously been tested. The delivery tube must be approximately central, and must on no account touch the side of the test-tube.

Pumping of the atmosphere to be tested shall be carried out with slow strokes (approximately 10 seconds per stroke), and be continued until the depth of colour developed (if any) is approximately equal to that of one of the standards. The bubbler is then removed and immediately compared, by transversely transmitted daylight, with the standard tube. Other methods of comparing the colours may be used such as a comparator with coloured glasses as standard, a photo-electric colorimeter, or an optical density meter.

The concentration of chlorine corresponding with the standard used and the number of strokes made is then read from the following table:

Number of strokes	Standard No. 1	No. 2	No. 3	No. 4
2	1/16,000	1/27,000	1/40,000	1/80,000
5	1/40,000	1/67,000	1/100,000	1/200,000
10	1/80,000	1/130,000	1/200,000	1/400,000
20	1/160,000	1/260,000	1/400,000	1/800,000
25	1/120,000	1/330,000	1/500,000	1/1,000,000

Where a test is required on air from a space not readily accessible, or where there is a possibility of a highly toxic concentration of chlorine being present, the air should be sampled from a distance. In the procedure described for this purpose the apparatus is connected with the space to be tested by means of glass tubing (approx. 0·25 in. bore) with rubber connections. When the sampling tube has been filled in this way with the atmosphere under examination, the bubbler is restored to the circuit, and a test is made in the usual manner. Approximately, one stroke of the pump is made per 12 feet of extension tube.

FIRST AID.—In cases of acute gassing with chlorine the patient should be removed to the fresh air and kept warm and at rest, pending the arrival of a doctor. If breathing is weak or stops, artificial respiration must be begun at once and continued for several hours even after it may seem to have failed.

Home Office

REPORT OF THE CHIEF INSPECTOR OF FACTORIES FOR THE YEAR 1938*

IN this Report H.M. Senior Medical Factory Inspector (Dr. J. C. Bridge) discusses the question of health risks in chemical industry.

LEAD POISONING.—Since lead poisoning became notifiable, nearly forty years ago, the cases have fallen from well over a thousand to less than one hundred per annum. Although only seven cases of lead poisoning in white lead works were reported, this number was greater than for many years. Five of these cases occurred at one factory where a new process had recently been started. In a number of instances it was found that lead paint was being applied by means of a spray, but, after representations had been made, the brush method was used.

MERCURIAL POISONING.—One case occurred in the manufacture of thermometers. The man, who had been employed for eight years, was a confirmed nail-biter. The other case was that of a female worker, aged 28, who had been employed for four months in assembling electric meters.

ARSENICAL POISONING.—In the three cases reported, dermatitis was present in addition to gastro-intestinal symptoms. One of the cases occurred in the manufacture of an insecticide containing calcium arsenate, and the other two in the manufacture of sheep dip containing sodium arsenite.

ANILINE POISONING.—Four of the nine reported cases were unusually severe, necessitating absence from work for two or three weeks or longer; aniline oil was responsible for two of these cases, *p*-nitro-chlorobenzene vapour for the third, and *p*-toluidine for the fourth. In this last case the methaemoglobinaemia called for a blood transfusion. The remaining five cases, which were slight, were caused by trinitrotoluene at a shell-filling factory.

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 2s. 2d.

Investigation of a case of "leucopenia" showed that the boy in question, aged 17, had been employed as a cellulose sprayer for about 14 weeks, and that during part of his time he had used a cellulose solution containing as much as 30 per cent. of benzene, while the other cellulose paint which he had sprayed contained toluene.

HYDROGEN ARSENIDE POISONING.—Three cases of toxic jaundice were caused by arseniuretted hydrogen evolved from cadmium residues in a chemical works.

CHLORINATED NAPHTHALENE WAX.—Three fatal cases of jaundice were investigated in which there was exposure, in varying degree, to fumes from chlorinated naphthalene wax.

CHROME ULCERATION.—The number of notified cases increased from 101 in 1937 to 115 in 1938, the main increase being in connection with the process of anodic oxidation. An unusually high number of cases occurred at one factory where there was some deterioration in the plant. New methods of crystallisation, to avoid handling the chrome products, were considered, and a fortnightly, instead of a monthly, medical examination of the workers was instituted.

EPITHELIOMATOUS ULCERATION.—The relatively low figures for gas works (12 cases with one death) may be due to a more prolonged contact with the carcinogenic agent being necessary than when there is tar distillation. The comparative figures of 1934 to 1938 appear to bear out the suggestion that there is a tendency in recent years for the disease to manifest itself at an earlier age and after a shorter period of service than formerly, but it is more probable that periodical medical examination and ray treatment leads to a number of cases that have not yet assumed malignancy being included in the returns.

DANGEROUS DUSTS.—Not many years ago asbestos dust, which is now recognised as highly dangerous, was regarded as innocuous. On the other hand, substitution of a relatively harmless dust for a harmful one is a valuable means of protection. It is gratifying, therefore, to be able to report excellent progress in the substitution of alumina for flint in one of the processes of the pottery industry.

DYE WORKERS' BLADDER CANCER.—Five cases of papilloma of the bladder in workers engaged in synthetic dye manufacture came to the knowledge of the Department. As usual, most of the workers had come into contact with more than one dyestuff intermediate, but three were known to have had substantial contact with β-naphthylamine. In two cases no contact with this chemical could be traced, both men being employed mainly, if not solely, in the manufacture of auramines, which involved contact with various intermediates derived from dimethylaniline. The onset of the disease in all cases occurred prior to 1938, and in one case as early as 1931.

POISONING BY FUMES AND GASES.—Of the 190 cases reported, 98 were due to carbon monoxide, 10 to hydrogen sulphide, 17 to chlorine, and 14 to nitrous fumes. Three cases of ammonia poisoning were caused by an escape of fumes from refrigerator plant. One case of gassing by trichloroethylene was due to escape from a dry-cleaning plant, and a case of phosgene poisoning was probably due to formation of phosgene while a fire was being extinguished with a patent extinguisher. During the past few years several complaints have been received about the irritating nature of acrolein fumes intermittently evolved, and at one large foundry simple canister respirators have been worn four or five times a day for ten minutes at a time with satisfactory results.

DERMATITIS.—There were 2195 cases of dermatitis voluntarily reported, as compared with 1985 cases in 1937. Among the new causative agents is ultramarine, to which two cases were attributed. In each case the length of exposure was four years.

A suitable "barrier substance" against dermatitis has been found, but is being put to further practical tests in various factories before the prescription is issued.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1938

THE Government Analyst (Mr. Kenneth Wallis) reports that the number of samples and specimens examined for 27 Government Departments and various private firms and individuals was 8939 as compared with 8774 in 1937. These included 1994 samples from the Director of Medical Services, 1876 from the Comptroller of Customs, and 2035 exhibits from the Commissioner of Police.

POISONING CASES.—Eighteen cases, involving the examination of fifty exhibits, were received. The principal poisons found were corrosive sublimate, acriflavine, tartar emetic, Jeyes' fluid, zinc sulphate and potassium cyanide.

OBEAH.—From time to time cases of obeah (witchcraft) are still brought before the Courts. Thirty exhibits were submitted in connection with four cases. They included skull, powdered skull, vegetable powders, oil, mercury, copper sulphate, resin, dried manure and bone.

FOOD AND DRUGS.—Of the 4876 samples submitted under the Food and Drugs Ordinance, 415 were reported as adulterated and prosecutions followed. The percentage of adulteration was 8·5 as compared with 6·7 in 1937.

Milk.—Of 4212 samples examined, 399 were adulterated, 220 being deficient in solids-not-fat and 179 in butter-fat. Special raids are unexpectedly carried out by the Police Department and Public Health authorities on Sundays and public holidays and after official hours. The number of samples so analysed was 1036, of which 102 were adulterated, the percentage adulteration being 10·1 as compared with 9·4 on ordinary weekdays.

British Standards Institution

HANDBOOK OF INFORMATION*

INCLUDING ANNUAL REPORT, 1938–1939

THIS Handbook, published July, 1939, contains 115 pages, and includes a Chart of Organisation, General Council, Divisional Councils, Industry Committees and Aims and Objects of the Institution.

Also, lists of British Standard Methods of Test used in B.S. Specifications. New and Revised British Standards in Course of Preparation. British Standards: Numerical List; Subject Index. Dominion and Foreign Standards Organisations. Government Department Co-ordinated Specifications.

THE following Table has been issued:†

NO. 860—1939. TABLE OF APPROXIMATE COMPARISON OF HARDNESS SCALES.

In view of the fact that to an increasing extent the "Brinell," "Diamond Pyramid" and "Rockwell" tests are being used in different works or laboratories for measuring the hardness of the same material, there has been a general demand for some means of correlating the most used A, B and C scales of the Rockwell test with those of the other tests.

Investigations show that there can be no general theoretical relationship between these scales, and empirical formulae devised from experiments only hold closely for materials of approximately similar composition and in a given condition. *Variations* in the empirical relationships result if the conditions as regards composition, heat-treatment and cold work differ appreciably, and also if different loading ratios are selected in the Brinell test. On the other hand, groups of materials similar as regards composition, cold work, etc., when tested by any of the above methods, may give fairly close comparisons.

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* British Standards Institution. Publications Dept., 28, Victoria Street, London, S.W.1. July, 1939. Price 1s. 6d.

† Publications Department, 28, Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

The Table is therefore a general approximation. It is issued solely as an indication of the order of the relationship between the three systems of Hardness Readings, and must not be used as a standard for the conversion of hardness values given on one scale in any British Standard to those of another scale.

The Diamond Pyramid Scale has been taken as the basis of reference, and the most probable comparative values have been adopted from published experimental results.

This Table requires reference to the following British Standards:

No. 240. Methods and Tables for Brinell Hardness Numbers.
No. 427. Tables of Diamond Pyramid Hardness Numbers.
No. — *Direct Reading Hardness Test (Rockwell Principle).

* In preparation.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Colorimetric Determination of the Preservative Value of Hops. A. A. D. Comrie. (*J. Inst. Brewing*, 1939, **45**, 336–341.)—Ferric chloride has been found to possess certain disadvantages as a colour-matching agent in the colorimetric determination of the preservative value of hops, and a 0·001 *N* solution of iodine with potassium iodide is proposed in its place. The method has been re-studied with this solution as colour-matching agent, and a slightly modified procedure is described. In determining the relation between colour value, in terms of 0·001 *N* iodine, and preservative value it has been found that the colour value is proportional to an average of $\alpha + \beta/5{\cdot}5$ for some standard English varieties (where α and β represent α- and β-resins), and to an average of $\alpha + \beta/4{\cdot}4$ for some American varieties, the actual value varying slightly from hop to hop. For "Brewers' Gold," the only member of the new hybrids to be studied, the colour value is proportional to $\alpha + \beta/3$. Three distinct standards are therefore proposed for use in the colorimetric determination of the preservative values, expressed as $10(\alpha + \beta/3)$, of these three classes of hops. The effects of using such fixed standards on the accuracy of the method, as applied to different hops with varying β-resin content, is discussed, and it is pointed out that the errors involved will be small. The method is rapid and requires only the simplest of apparatus and reagents. To obtain the hop colour a 5 per cent. extract in 90–100 per cent. alcohol is made, 1 ml. is diluted to 50 ml. with alcohol, 15 ml. of this are placed in a 25-ml. measuring flask, 1 ml. of uranium nitrate solution (1 per cent. in alcohol with 0·5 per cent. of pyridine) is added, and the mixture is made up to the mark with alcohol. This gives a 0·05 per cent. solution, which is generally convenient for matching with the standard colour value, *i.e.* the colour given by 0·8 mg. of hop resin or its equivalent as matched with 0·001 *N* iodine. If the calibration value of the hop colorimeter tube is *x*, the concentration (per cent. of hop) of the hop solution tested is C, and the depth (in mm.) of the hop solution tested is D, the preservative value of the hop is given by the general expression $80x/\mathrm{C.D}$. This value will be approximate, for it is based on average results, from which individual hops will deviate, from the brewers' point of view; however, an approximate measure is all that is needed. D. R. W.

Preliminary Investigation of the Lichthardt Test for the Detection of Caramel in Cider Vinegar and Distilled Vinegars. F. E. Cook and H. Miller. (*J. Assoc. Off. Agr. Chem.*, 1939, 22, 588–593.)—The Lichthardt test (*J. Ind. Eng. Chem.*, 1910, 2, 389) was applied to pure cider vinegars and distilled vinegars to which caramel had been added. The reagent was prepared as follows:—Exactly 4 ml. of sulphuric acid (sp.gr. 1·84) were added to 9·8 g. of tannic acid dissolved in 294 ml. of water, and the mixture was diluted to 490 ml. with water. This reagent (5 ml.) is added to 5 ml. of vinegar and, according to the original method, the mixture should be heated gently until the precipitate first formed is nearly dissolved and then set aside for 12 hours. A brown precipitate adhering closely to the bottom of the test-tube indicates caramel; a flocculent precipitate is disregarded. Experiments showed that often no precipitate was formed whether the vinegar contained caramel or not, and the effect of variations in the degree of heat applied was investigated. Some caramels gave no immediate precipitate when the reagent was added. Uncontrolled heating gave unsatisfactory results, and temperatures of 50° C. and above interfered with the formation and settling of the precipitate. Temperatures up to 48° C., maintained for not more than 4 minutes, did not interfere with the formation and settling of the precipitate, but showed no specific advantage over temperatures of 30° to 40° C. Some vinegars which had darkened in colour after standing for 3 or 4 months gave slight precipitates where previously they had given none. One sample gave a slight precipitate under all conditions of the test, and the results of Amthor's test for caramel were also inconclusive. A precipitate allowed to form undisturbed would spread itself over the side walls and bottom of the tube, but a slight twist of the tube would cause it to settle to the bottom. No precipitate adhering firmly to the walls was noted, and very little difference was found between precipitates obtained from vinegars containing caramel and those obtained in absence of caramel. The precipitate produced when caramel had been added to the vinegar was slightly less flocculent and less easily disturbed than the smaller precipitate produced when no caramel had been added. It may be the intention of the original method that the mixture of vinegar and reagent should not be heated unless a precipitate has formed. The method is considered sufficiently promising to warrant further investigation of the conditions in which the precipitates can be distinguished. A. O. J.

Observations on the Colorimetric Method for the Determination of Vanillin. A. L. Curl and E. K. Nelson. (*J. Assoc. Off. Agr. Chem.*, 1939, 22, 684–688.)—Results obtained by the colorimetric method for the determination of vanillin (*Methods of Analysis, A.O.A.C.*, 1935, 307) were much higher than those obtained gravimetrically, and a colorimetric determination made upon the residue from the gravimetric extraction showed that a substance that was not vanillin reacted with the reagent. Similar discrepancies were found with extracts of Bourbon, Java, Mexican, South American and Tahiti vanilla beans as with the Puerto Rico vanilla first used. The effect of changes in the ratio of neutral to basic lead in the basic lead acetate reagent was investigated, and it was found that the ratio should not be much greater or less than 3 to 1. A ratio of 6·3 to 1 was unsatisfactory, especially if the vanilla contained much resin, since the interfering substances were not completely precipitated and high results were obtained. On the other hand, a ratio of 1·2 to 1 caused precipitation of some vanillin and led to low results. The basic lead acetate used for preparation of the reagent should therefore be assayed, and if the ratio of neutral to basic lead is much greater than 1 to 1, the material should be rejected. The preservation of standard vanillin solutions used in the colorimetric method was investigated. A standard vanillin solution kept in a partly filled bottle increased in apparent strength, probably by oxidation. A full bottle kept in a refrigerator gave the same results as the fresh solution. Folin and Denis (*J. Ind. Eng. Chem.*, 1912, **4**, 671; Abst., ANALYST, 1912, **37**, 501) state that in the colorimetric method, with the standard set at 20 mm., no readings should be accepted as final if they fall much outside the limits of 15 to 30 mm. A 20 per cent. sodium carbonate solution, as recommended by Snell (*Colorimetric Methods of Analysis*, 1937, **2**, 86), was found preferable to the saturated solution. In making the gravimetric determinations, extraction with ammonia (designed to separate vanillin from coumarin) was omitted. Petroleum spirit extracts of the crude vanillin residues were made, and the insoluble impurities were deducted. When the extraction with ammonia was not omitted the results were, on the average, about 2·1 per cent. lower. A. O. J.

Volatile Oil in Sage. J. F. Clevenger. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 683–684.)—Most of the sage leaves used in the United States are grown in Jugoslavia and imported from Trieste. These are known as Dalmatian sage (*Salvia officinalis*). A certain amount of Greek sage (*Salvia triloba*) is imported from Athens. The characteristics of the volatile oils of the two species determined by the methods outlined in *Methods of Analysis, A.O.A.C.*, 1935, 447 *et seq.*, are as follows, the first number (*a*) referring to Dalmatian and the second (*b*) to Greek sage:—yield of volatile oil (ml. per 100 g.), (*a*) 1·2 to 2·3; (*b*) 2·1 to 2·6; sp.gr. (25°/25° C.), (*a*) 0·917 to 0·937; (*b*) 0·907 to 0·918; $[\alpha]^{25}_{D}$, (*a*) +3·8 to +13·5; (*b*) −4·1 to −21·0°; n^{20}_{D}, (*a*) 1·461 to 1·469; (*b*) 1·466 to 1·473; acid value, (*a*) 0·9 to 3·5; (*b*) 0·57 to 1·75; ester value, (*a*) 10·8 to 28·74; (*b*) 13·0 to 25·2. The difference in optical rotation of the two kinds of oil provides a valuable means of distinguishing them. Coarsely-ground sage leaves when stored in an open shallow pan in the laboratory for 7 months lost about 25 per cent. of their content of volatile oil. A. O. J.

Preservation of Pharmacopoeial Paraldehyde: Detection of Resorcinol. J. S. Toal. (*Pharm. J.*, 1939, **143**, 226–227.)—In an investigation on the effect of preservatives on the keeping properties of paraldehyde, it was necessary to test for the presence of resorcinol. This was successfully accomplished by a modification of Carrobio's test (*Boll. chim. farm.*, 1906, 365; *Yearbook Pharm.*, 1907, 133). Ten ml. of the paraldehyde to be tested were shaken for about a minute with 2 ml. of 0·1 per cent. zinc sulphate solution to which 4 drops of conc. ammonia solution had been added. After standing for half-an-hour the aqueous layer separated with a deep-blue colour when resorcinol was present. Under these conditions the test is sensitive to 10 parts of resorcinol per million. F. A. R.

Verbenin, a Glycoside from *Verbena officinalis*, which Promotes Milk Secretion. K. Kuwajima. (*Tohoku J. Exp. Med.*, 1939, **36**, 30–43.)—A glycoside, to which the name "verbenin" has been given, has been obtained from the powdered root of *Verbena officinalis* L. by extraction with hot ether. The aqueous solution of the residue obtained on cooling the hot ethereal solution was filtered and evaporated, and the residue was taken up in hot alcohol. On diluting the alcoholic solution there separated a substance which by fractional crystallisation from absolute alcohol could be separated into a major portion crystallising in platelets, and a minor portion forming needle-shaped crystals. The former is chiefly responsible for the action of the root in promoting the secretion of milk. The m.p. of the plate-shaped crystals, which constitute the new substance verbenin, is 179° C. The needle-shaped crystals, which appear to be identical with the verbenalin of Bourdier (*cf. Abderhalden, Biochemisches Handlexikon*, Berlin, 1911, 2, 681) and of Holste (*Z. exp. Path. u. Therap.*, 1918, 19, 483), melt at 177° C. Both glycosides, which have a very bitter taste, dissolve easily in water and absolute alcohol, sparingly in ether, and very difficultly in chloroform, the aqueous solutions being neutral. Both reduce Fehling's solution and ammoniacal silver nitrate solution on warming, particularly after treatment with hydrochloric acid, but not in the cold. On prolonged boiling with dilute sulphuric acid both give bright yellow amorphous precipitates, and when they are heated with acetic acid and phenylhydrazine light red-brown precipitates gradually separate. Injected into guinea-pigs, small quantities of verbenin have an exciting action, and large quantities a paralysing effect, on the sympathetic nerve endings of the mucous membrane, the heart, and the blood vessels. In very large quantities the glycoside paralyses the central nervous system. With milk-yielding animals quantities of verbenin which do not cause any other appreciable changes bring about a marked increase in milk secretion, which continues for some time. After entry into the blood verbenin appears to become fixed and gradually destroyed in certain tissues. E. M. P.

Exalgin, its Identification and Detection in Mixtures. A. Denoël. (*J. Pharm. Belg.*, 1939, 21, 691–695, 709–711.)—Exalgin (*N*-methyl acetanilide) is frequently present in mixtures containing also one or more of the other antipyretics, acetanilide, phenacetin, antipyrine and pyramidone, and it has been difficult hitherto to detect its presence in such instances. The behaviour of a solution of exalgin towards various reagents was therefore studied, and compared with that of the four other compounds. In general, phenacetin and acetanilide did not give precipitates with the reagents used, whereas antipyrine gave precipitates with all, pyramidone with most, and exalgin with about two-thirds. The compounds obtained by treating exalgin with potassium ferrocyanide, gold chloride, iodine in acetic acid, potassium iodate (or bromate) in hydrochloric acid, and Reinecke's salt formed crystals of characteristic appearance when examined under the microscope. These reagents are therefore suggested for identifying exalgin. Exalgin can be separated from phenacetin and acetanilide by extracting 1 g. of the mixture with 5 ml. of cold water. The solubilities of phenacetin, acetanilide and exalgin are respectively 1 in 1400, 1 in 230 and 1 in 60. Exalgin can be characterised in the filtrate by any of the tests mentioned above (with the exception of the last), which give negative responses with phenacetin and acetanilide. In the examination of mixtures of exalgin and antipyrine it is essential to remove all the antipyrine before attempting to test for exalgin. This can be done in three different ways. In the first method 10 ml. of a solution containing 0·5 g. of the mixture are shaken with 20 ml. of Lugol's solution,* and filtered after standing for 30 minutes. The filtrate is decolorised with sodium thiosulphate solution, made alkaline and extracted three times with ether. The combined ethereal extracts are filtered and evaporated. The residue contains no antipyrine. In the second method a solution of 0·2 g. of the mixture in 10 ml. of cold water is shaken with 50 ml. of 1 per cent. picric acid solution for 5 minutes and filtered. The filtrate is made alkaline and extracted with ether, and the ethereal extract is evaporated. The residue obtained is used for the test. In the third method a solution of 0·2 g. of the mixture in 10 ml. of water and 2 ml. of 10 per cent. sulphuric acid is shaken with 20 ml. of 40 per cent. ammonium thiocyanate solution for 5 minutes and the mixture is filtered through a sintered-glass filter. The filtrate is made alkaline and extracted with ether, and the extract is evaporated. The residue is used for the test. Of these methods, the first and the third are preferred. Exalgin is detected in the residues by any of the five reagents described above. When exalgin occurs in a mixture with antipyrine and pyramidone, it can be freed from both these substances with Lugol's solution as described above, and the residue used for testing for exalgin. F. A. R.

Determination of Amidopyrine in Presence of Antipyrine and Caffeine. F. C. Sinton and F. A. Rotondaro. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 678–680.)—Caffeine and antipyrine can be extracted quantitatively with chloroform from an aqueous solution containing 3·5 to 5 per cent. by weight of sulphuric acid. The aqueous residue is then made ammoniacal, and the amidopyrine is completely extracted with chloroform. The following procedure was found satisfactory for a solution containing 3 g. of amidopyrine, 2 g. of antipyrine and 0·5 g. of caffeine in 100 ml.:—The sample (10 ml.) was mixed with 5 ml. of sulphuric acid (10 per cent. by weight) and extracted with five 25-ml. portions of chloroform. The extracts were washed with 5 ml. of 3·5 per cent. sulphuric acid. The residue, after removal of chloroform by evaporation, was dried at 80° to 100° C. for 10 minutes and weighed. The combined aqueous residue and washings were made alkaline with ammonia, and the amidopyrine was extracted with chloroform, dried at 80° to 100° C. and weighed. If the original aqueous solution is saturated with anhydrous sodium sulphate before extraction, the concentration of acid necessary to effect complete separation is higher (10 per cent.) but less critical. The sodium sulphate appears to depress the ionisation of the acid, and the 5 ml. of acid added should contain 30 per cent. by weight of sulphuric acid. This method might presumably be applied to the determination of amidopyrine in admixture with other drugs. A. O. J.

Estimation of Small Quantities of Arsanilic Acid in Tryparsamide. C. A. MacDonald and J. G. Reynolds. (*Pharm. J.*, 1939, **143**, 222.)—The method proposed for the estimation of arsanilic acid in tryparsamide is a modification of the limit test described in the B.P. Addendum, 1936. Exactly 0·5 g. and 1·0 g. of tryparsamide are weighed into two test-tubes and dissolved in 6·0 ml. of water. Each tube is cooled below 5° C. and 2·5 ml. of 4 per cent. sodium nitrite solution are introduced into each, followed by 5 ml. of 10 per cent. hydrochloric acid. The contents of each tube are mixed and poured into 10 ml. of a cooled solution of β-naphthol, and the colour is measured in red units in the 1-cm. cell of a Lovibond tintometer. The amount of arsanilic acid present is calculated from a graph prepared in a similar manner with the aid of solutions of pure atoxyl of known strength. The colour develops its maximum intensity within a few minutes and remains unchanged for several hours. The quantity of sodium nitrite is the critical factor, since increasing amounts augment the colour produced from a fixed amount of arsanilic acid, whereas an insufficient amount gives almost the same colour when the amount of arsanilic acid is increased many fold. Satisfactory results were obtained with tryparsamide containing arsanilic acid of the order of 0·05 per cent. A serious anomaly in the Pharmacopoeial test was revealed, for whereas a sample containing 0·02 per cent. of arsanilic acid will just fail to satisfy the official test, a sample containing 0·05 per cent. will apparently fulfil the official requirements. The reason for this is that insufficient sodium nitrite is employed in the B.P. test, and the full colour development does not take place in the tube containing the larger amount of tryparsamide, so that this may actually be paler in colour than the other tube containing the smaller amount.

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* A 5 per cent. solution of iodine in 10 per cent. potassium iodide solution.

F. A. R.

Riboflavin in Liver Extract.—G. E. Shaw. (*Pharm. J.*, 1939, **143**, 222–223.)—A fluorometric method of estimating lactoflavin after conversion into lumiflavin by irradiating its alkaline solution has been developed. Exactly 1 ml. of the liver extract to be tested is measured into a 50-ml. separating funnel and mixed with 1 ml. of *N* hydrochloric acid and then with 10 ml. of acetone. The mixture is repeatedly extracted with 10-ml. portions of chloroform, acetone being added when necessary, until the lower layer ceases to give a blue fluorescence when examined in "black light." The combined lower layers are repeatedly extracted with 5-ml. portions of water until no more fluorescing material can be removed. The chloroform solution is discarded. The aqueous extracts are combined, extracted with chloroform to remove any blue fluorescing material, and transferred to a distillation flask, together with the upper layer from the original extraction. Acetone is removed by heating at 35° to 40° C. under reduced pressure, and the solution is made just alkaline to phenolphthalein and diluted to 30 ml. It is then transferred to a shallow evaporating dish, mixed with an equal volume of *N* sodium hydroxide solution, and exposed to unfiltered ultra-violet light for a suitable time. (An S.500 Hanovia analytical lamp for 10 minutes at a distance of 18 in. was satisfactory.)

The irradiated solution is transferred to a 200-ml. separating funnel, made faintly acid to phenolphthalein by addition of a 20 per cent. solution of citric acid, and extracted with 10-ml. portions of chloroform until no more green fluorescing material is removed. The combined chloroform extracts are diluted to a suitable volume, and the fluorescence of 10 ml. is compared in a test-tube with standard lumiflavin tubes. To prepare these standards, a series of 10 dilutions of riboflavin, from 0·1 to 1·0 mg. per 100 ml., is made, 1 ml. of each is diluted with 4 ml. of water and 5 ml. of N sodium hydroxide solution, and the mixture is irradiated as described above. Each is then acidified to phenolphthalein and extracted with chloroform. The combined extracts are diluted to 20 ml., and 10 ml. are sealed up in non-fluorescent glass test-tubes. Figures varying between 6 and 1·8 mg. per 100 ml. were obtained for 8 preparations for oral administration, and 16 to less than 0·1 mg. in the same volume, for 11 parenteral preparations. F. A. R.

Biochemical

Distribution of Bromide and Chloride in Tissues and Body Fluids. E. G. Weir and A. B. Hastings. (*J. Biol. Chem.*, 1939, **129**, 547–558.)—Contradictory reports on the distribution of bromides between the blood and various body fluids and tissues after bromide administration having been published in the literature, a re-investigation of the problem was deemed desirable, and especially a critical examination of the methods used for determining bromides in such materials. The research involved the administration of sodium bromide to anaesthetised dogs and the subsequent analysis of blood, body fluids and tissues. Samples of blood and tissue were obtained and prepared for analysis according to the methods described by Hastings and Eichelberger (*J. Biol. Chem.*, 1937, **117**, 73), but an examination of the electro-titrimetric method used by Hastings and van Dyke (*J. Biol. Chem.*, 1931, **92**, 13) for the determination of bromides proved that the method was inaccurate when small amounts were present, owing to the fact that these workers used tungstic acid filtrates of cells which contained organic material capable of reacting with silver. The following modified method was therefore devised to overcome this difficulty:—The halides of the dried fat-extracted tissue (about 0·4 g.) obtained after the determination of water and fat, were converted into silver salts by digestion with excess of silver nitrate solution and nitric acid (*cf.* Sunderman and Williams, *J. Biol. Chem.*, 1931, **92**, 99). The mixture of silver halides formed was allowed to settle to the bottom of the Pyrex tube in which the digestion was carried out, and the supernatant liquid was drawn off by a pipette. The precipitate was washed with distilled water until the solution was free from silver. The digestion-tube was then attached to a series of three absorption vessels, and the washed silver halides were decomposed in the tube by adding 0·1 g. of manganese dioxide and 3 ml. of conc. sulphuric acid and boiling the mixture for 30 to 40 minutes. The mixture of chlorine, bromine, hydrogen chloride and hydrogen bromide produced was absorbed in 15 ml. of a 0·1 N sodium sulphite solution in 4 N sodium hydroxide solution contained in the receiving vessels. When the distillation was complete, the contents of the receivers were washed into conical flasks, neutralised to methyl orange with conc. nitric acid and treated with hot saturated barium nitrate solution to remove sulphate ions. The solution was made up to 100 ml. and filtered, and 50 ml. of the clear filtrate were used for the electrometric titration of the bromide. The subsequent procedure was identical with that described by Hastings and van Dyke, except that the titration was carried only to the bromide end-point. Total halides, and thus chlorides by difference, were determined by adding 3 ml. of water to the mixture remaining in the digestion-tube after decomposition of the silver halides, and adding a drop or two of potassium oxalate solution if the resulting solution was pink, followed by 3 ml. of 10 per cent. ferric alum solution. The silver ion was titrated with 0·02 *N* ammonium thiocyanate solution. When known amounts of bromide were added to tissues and body fluids, it was found that a slight end-point correction was necessary to yield correct results, but total halide recovery in tissues and body fluids was satisfactory without correction. The results obtained were uniformly consistent among themselves and in agreement with the recent results of Wallace and Brodie (*J. Pharmacol. and Exp. Therap.*, 1939, **65**, 220). F. A. R.

Colorimetric Estimation of Phosphorus in Complex Mixtures. G. Barac. (*Bull. Soc. Chim. Belg.*, 1939, **48**, LII–LIII.)—The colorimetric method devised by Bell and Doisy (*cf.* ANALYST, 1921, **46**, 13) for the estimation of the total phosphorus in biological fluids, has been found to give satisfactory results with faeces. The method is specific for phosphate phosphorus. With a Pulfrich photometer as little as 4γ can be measured in a 3-cm. cell, and up to 300γ in a 0·5-cm. cell. A loss of as much as 35 per cent. of the phosphorus was experienced when an attempt was made to decolorise simple aqueous solutions with animal charcoal, but the loss was avoided altogether by using a trichloroacetic acid solution. By suitable modifications it was found possible to apply the method to the estimation of phosphorus in different states of combination. The powdered dried faeces were extracted with chloroform to remove phospholipoids, and the residue was allowed to stand for several hours in contact with trichloroacetic acid. The filtrate, after being decolorised with animal charcoal, was used for the estimation of the total phosphate, whilst the amount of inorganic phosphate was measured in the solution obtained after igniting the trichloroacetic acid extract, and the amount of organic phosphate was obtained by difference. Lipoid phosphorus was estimated in the residue obtained by evaporating the chloroform extract, either after ignition or after hydrolysis with hot acid. The method fails to give satisfactory results with substances of the type of casein, for the sum of the phosphorus present in the three forms mentioned above did not amount to more than 50 per cent. of the total phosphorus. The remainder was characterised by its solubility in warm alkali solution and was estimated after oxidation with nitric-perchloric acid mixture. F. A. R.

Recent Investigations on Bilirubin. G. Barac. (*Bull. Soc. Chim. Belg.*, 1939, **48**, LIII–LIV.)—The simplest method of estimating bilirubin is direct colorimetric measurement in an alkaline solution, but the method suffers from the grave disadvantage that alkaline solutions of bilirubin are rapidly oxidised, even when prepared and stored in the dark. The oxidation was not inhibited by formaldehyde, thiosulphates, hydrosulphites or antioxidants, such as polyhydric phenols. It was found, however, that a small amount of ascorbic acid stabilised the alkaline solution, and this observation was applied with complete success to the colorimetric estimation of bilirubin. Thus the addition of 200 mg. of ascorbic acid to a solution of 5 mg. of bilirubin in 1 ml. of 0·01 *N* sodium hydroxide solution prevented any loss of colour during 72 hours. The use of such a solution also enabled the absorption spectrum in both the visible and the ultra-violet regions of the spectrum to be studied without difficulty. F. A. R.

Determination of Phenol and related Compounds in Tissues. W. Deichmann and H. W. Scott. (*Ind. Eng. Chem., Anal. Ed.*, **1939**, **11**, 423–424.)—The phenolic compounds in tissues have been separated into (1) volatile compounds, and (2) acidic, neutral and basic non-volatile ether-soluble compounds. The phenolic substance in each was estimated colorimetrically as phenol. An aqueous extract of at least 20 g. of the ground tissue was treated with Folin–Wu reagent, allowed to stand for at least 15 minutes to precipitate the proteins, and filtered. A measured volume of the filtrate was acidified in a 250–ml. distillation flask with conc. hydrochloric acid (1 ml. per 25 ml. of filtrate) and steam-distilled at constant volume in an all-glass apparatus into 2 ml. of 4 per cent. sodium hydroxide solution (A). The distillate, measuring approximately 270 ml., was concentrated on a hot plate to 8 or 10 ml. After concentration of the distillation residue to 100 ml. and filtration, the three non-volatile fractions were separated as follows: *Acidic.*—The solution was extracted five times with ether, and the combined ethereal solutions were extracted with 5 ml. of (A) and 20 ml. of water. If the extract was not alkaline, the extraction was repeated with the same solution after addition of another 2 ml. of (A). The ethereal solution was extracted four times more with 0·5 per cent. sodium hydroxide solution (B), and the combined alkaline extracts, after removal of the remaining neutral compounds by two extractions with ether, were neutralised (to litmus) with 10 per cent. hydrochloric acid (C) and evaporated to 5 or 8 ml. *Neutral.*—The original ethereal solution, together with the two ethereal extracts of the alkaline solution, were mixed with 5 ml. of water containing a drop of (C), and the ether was evaporated on a water-bath kept below 80° C. *Basic.*—The acid solution which was previously extracted with ether was made just alkaline to litmus with (A), and extracted five times with ether, and the combined extracts were treated in the same way as the previous ethereal extract. The phenol in all four fractions was determined as follows:—The concentrated solution was filtered into a graduated 50-ml. cylinder and made up to 20 ml. with the washings of the flask and filter. To this, and to 20 ml. of standard phenol solution, were added 1 ml. of a 25 per cent. solution of sodium acetate in a 0·5 per cent. (aqueous) solution of gum acacia, 2 ml. of Moir's reagent (D) and, after 1 minute, 4 ml. of 20 per cent. sodium carbonate solution (E). (The reagent (D) was prepared daily from a solution of 1·5 g. of *p*-nitroaniline in 40 ml. of (C), diluted to 500 ml. Seventy-five ml. of this were treated with 0·75 ml. of 10 per cent. sodium nitrite solution.) After 3 minutes the solutions were compared colorimetrically. The neutral fraction, which was very weak, was compared in test-tubes with a series of standards containing from 0·000 to 0·015 mg. of phenol in 20 ml. For the other fractions, 20 ml. of the standard solution contained 0·015 mg., and a colorimeter was used. E. B. D.

Carbamido Diacetyl Reaction. A Test for Citrulline. W. R. Fearon. (*Biochem. J.*, 1939, **33**, 902–907.)—A method of detecting citrulline (α-amino-δ-carbamidovaleric acid) in proteins is of some importance biochemically in relation to nitrogen metabolism, since citrulline is an intermediate between ornithine and arginine. A number of aldehydes that yield coloured condensation products with ureas were rejected as reagents for citrulline on account of their giving even more intensely coloured products with tryptophane. Diacetyl in strongly acid solution, however, yielded, with substituted ureas, products which were converted into orange or red pigments on careful oxidation, and tryptophane and substituted guanidines did not give colours with this reagent. The guanidines gave colours with diacetyl in alkaline solution only. Diacetyl monoxime was found to be superior to diacetyl itself in the test, and the oxidation was most conveniently carried out with potassium persulphate. About 2 ml. of the protein solution are treated with at least 4 ml. of conc. hydrochloric acid and 3 to 5 drops of 3 per cent. aqueous diacetone monoxime solution. The mixture is boiled for 30 seconds, allowed to cool, and then carefully oxidised by adding 1 to 3 drops of 1 per cent. potassium persulphate solution or of 0·01 per cent. hydrogen peroxide solution. A carmine red colour develops if citrulline or a similar carbamido-compound is present. The colour deepens on standing or on warming gently. A slight excess of the oxidising agent rapidly bleaches the pigment in hot solution. The reaction will detect as little as 0·01 per cent. of citrulline. The time of boiling must be reduced when large amounts of carbohydrate are present, as, for instance, with dried milk powder, for such substances readily form furfuraldehydes which react with tryptophane giving violet pigments. It is useful to check the absence of this reaction by making a control test without the addition of diacetyl monoxime, though it should be noted that some samples of caseinogen from sour milk may contain diacetyl or acetoin, and so give a positive reaction even when no reagent has been added. Urea itself gives a bright yellow colour, deepening to orange on oxidation, and the reaction will detect 0·1 mg. of urea in 2 ml. of solution. Semicarbazide gives a colour in absence of an external oxidising agent, and the pigment gradually separates out as a dark red precipitate. Compounds that behave like citrulline are: methylurea, butylurea, phenylurea, β-naphthylurea, dimethylurea (symmetrical and unsymmetrical), allantoin, and all higher proteins examined (ovalbumin, seralbumin, seroglobulin, caseinogen, lactalbumin, fibrin, edestin, gluten, mucin). Commercial peptones and gelatins give the reaction with varying degrees of intensity. The test is negative with ammonium salts, hydrazine, carbamate, cyanate, acetamide, acetylurea, diphenylurea (unsymmetrical), guanidine, methylguanidine, creatine, creatinine, glycocyamine, uroxamic acid, uric acid, indole and all amino-acids examined other than citrulline. F. A. R.

Colorimetric Estimation of Tocopherol (Vitamin E). III. Estimation of Tocopherol in Blood-serum. A. Emmerie and C. Engel. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 895–902.)—Tocopherol, like vitamin A, cannot be extracted directly from serum by shaking with ether. Digestion with a solution of alkali cannot be employed to convert the tocopherol into an ether-extractable form, as considerable loss of activity occurs, the loss being greater the higher the temperature, the longer the treatment, and the stronger the alkali solution employed. Although tocopherol is stable to heating with hydrochloric acid, digestion of the serum with pepsin and hydrochloric acid did not effect recovery of added tocopherol. The following procedure was therefore adopted:—To 10 ml. of the serum in a 250-ml. separating funnel were added, with gentle shaking after each addition, 5 ml. of aqueous 0·2 N potassium hydroxide solution, 15 ml. of

37 per cent. formaldehyde solution (neutralised to phenolphthalein) and 15 ml. of ethyl alcohol. Fifty ml. of peroxide-free ether were then added, and the mixture was thoroughly shaken and allowed to stand. The aqueous layer was extracted twice more with 50 ml. of ether after the addition of 10 ml. of ethyl alcohol each time. The combined ethereal extracts were washed first with 25 ml. of 2 per cent. potassium hydroxide solution, then with 25 ml. of 1 per cent. sulphuric acid, and finally several times with water. The extract was dried over anhydrous sodium sulphate, mixed with 10 ml. of benzene, and evaporated under reduced pressure in an atmosphere of carbon dioxide. A further 10 ml. of benzene were added to the residue in the flask, and the mixture was again evaporated. The residue (a very small drop) was taken up in 5 ml. of pure benzene and filtered through a column (30 × 12 mm.) of purified "Floridin XS" earth (*cf.* ANALYST, 1939, **64**, 446). The column was washed with 25 ml. of benzene and the filtrate evaporated under reduced pressure. Acetyl-tocopherol is also extracted by this procedure. The residue in the flask was then dissolved in 5 ml. of the reagent mixture (1 ml. of dipyridyl solution, 1 ml. of ferric chloride solution and 5 ml. of benzene are made up to 25 ml. with ethyl alcohol), and the colour of the mixture was measured after 10 minutes in a Pulfrich photometer (*cf.* ANALYST, 1939, **64**, 216). The recovery of tocopherol, added in amounts of from 25 to 272γ to 10 ml. of serum, was 98 to 100 per cent. Applied to the serum of different groups of vitamin E-deficient rats (checked biologically), the method showed that administration of tocopherol or of acetyl-tocopherol gave rise to an increased tocopherol-content of the serum. It should be noted that acetyl-tocopherol does not react with the reagent prior to hydrolysis, which was effected by heating at 72° to 74° C. with methyl alcoholic potassium hydroxide solution for 10 minutes, diluting with water and extracting with three 50 ml.-portions of ether. In estimating the acetyl-tocopherol content of an unknown sample, a compromise has to be sought between the quantity of alkali necessary for saponification and the concentration necessary to reduce destruction of the tocopherol to a minimum. F. A. R.

Colorimetric Determination of Nicotinic Acid with 1-Chloro-3.4-dinitrobenzene. M. Covello. (*Boll. Soc. Ital. Biol. Speriment.*, 1938, **13**; *Chim. e Ind.*, 1939, **21**, 493.)—A method for the determination of small quantities of nicotinic acid in biological materials depends on the reaction between 1-chloro-3.4-dinitrobenzene with substances containing a pyridine nucleus, to give products which with sodium hydroxide form derivatives with an intense red colour. The material containing nicotinic acid is fused with 1-chloro-3.4-dinitrobenzene for half-an-hour at 160° C. The intensity of the resulting colour can be measured in a colorimeter with a photo-electric cell. The author has used the method for determining nicotinic acid in urine. E. M. P.

Bacteriological

Microbiological Examination of Frozen Egg Products. R. Schneiter. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 625–628.)—The presence of large numbers of viable organisms in frozen egg products indicates the use of poor quality stock, unsatisfactory manufacturing processes or insanitary plant conditions. A high incidence of coliform organisms and haemolytic types may, in addition, be a danger to health. For the sampling of the canned material it is recommended that three cores be removed from the container by means of a sterile electric drill. The thawed material (5 g.) is transferred under aseptic conditions to a glass-stoppered bottle containing 45 g. of sterile physiological saline solution and a tablespoonful of glass shot to promote thorough distribution by shaking. From this tenfold dilution serial dilutions may be made from one-hundredth to one-hundred-millionth concentration. Duplicate inoculations are made on nutrient agar or dextrose agar plates with 1-ml. portions of dilutions from one-thousandth to one-millionth concentration, one set being incubated for 3 days at 20° to 30° C. and the other for 3 days at 37° C. The plates incubated at the lower temperature give the higher counts. To determine the incidence of coliform organisms, fermentation tubes of lactose broth are inoculated with 1-ml. portions of dilutions of a tenth to a hundred-millionth concentration and incubated at 37° C. for 24 to 48 hours. From all lactose broth cultures yielding gas, streak cultures are made on Levine's eosin and methylene blue agar plates and incubated at 37° C. for 24 to 48 hours. Nutrient agar cultures are prepared by inoculation from colonies of the coliform type and are incubated for 24 hours at 37° C., and these purified cultures are subjected to Kovac's test (indol production), the methyl red and the Voges–Proskauer tests, and Koser's test (utilisation of sodium citrate as the sole source of carbon). Haemolytic types are isolated by inoculating Petri plates with 1-ml. portions from dilutions of one-hundredth to one-millionth concentration. Veal infusion agar containing 6 per cent. of defibrinated horse, sheep or rabbit blood is poured over the plates. The agar is cooled to 40° C., and the blood (0·6 ml. per 10 ml. of medium) is added immediately before pouring. The plates are incubated for 24 hours at 37° C. For counts of anaerobic organisms, tubes of chopped meat medium are inoculated with 1-ml. portions of dilutions from a tenth to a hundred-thousandth concentration and incubated at 37° C. for 3 days. Direct microscopical counts may be made on dried smear preparations of 0·01 ml. of the tenth or hundredth dilutions spread over an area of 1 sq.cm. Veal infusion agar is made by infusing 500 g. of lean veal with a litre of water in the refrigerator overnight, straining, removing fat, and adding 1 per cent. of peptone (Difco), 0·5 per cent. of sodium chloride and 1·5 per cent. of agar. The reaction of the medium is adjusted to *p*H 7·6. To prepare Holman's cooked meat medium, 500 g. of ground fresh lean beef is infused overnight in the refrigerator with a litre of water, 5 g. of bacto-peptone are added to the heated strained infusion, and then, after filtration of the mixture, 5 g. of sodium chloride are added. Normal sodium hydroxide solution is added until the medium is alkaline to phenolphthalein, and the liquid is re-heated and filtered. The pressed-out beef remaining from the infusion is distributed into tubes, approximately 2 g. being placed in each with 10 ml. of the cleared alkaline broth. The final reaction after sterilisation should be *p*H 7·2 to 7·4. Before use the tubed medium is boiled for at least 10 minutes and cooled quickly to expel adsorbed oxygen. Dextrose agar is made by adding 1 per cent. of dextrose to standard nutrient agar. The other media and tests mentioned are those described in *Standard Methods of Water Analysis*, American Public Health Association, 8th Ed., 1936. A. O. J.

Lobsters and Gastro-Enteritis. Some Experiments on Cooking and Sterilisation. H. M. Royds Jones. (*Lancet*, **1939**, **14** (ii), 738–9.)—Two outbreaks were previously described by the author, the first involving 152 and the second 49 patients. Investigation of the last one revealed the fact that the lobsters were of large size and were placed in boiling water and cooked for 40 minutes, after which the claws were cut off, the body was split longitudinally, the gut removed by the cook's fingers, and the body was cut up into portions for service. It is suggested that the contents of the gut were not completely sterilised by the process of cooking, and that the cook's fingers became soiled by the contents of the gut and conveyed the specific micro-organisms to the fleshy parts. To test this point, six lobsters from the same batch were cooked in the same way, and the contents of the gut were examined bacteriologically. *B. coli* and *B. proteus* were isolated, proving that complete sterilisation was not effected. A similar test was carried out by Professor Eyre, and *B. coli*, *B. proteus* and *B. aerogenes* were again recovered. Experiments were then made to ascertain the length of time required for boiling in order to secure sterilisation of the contents of the gut of lobsters weighing 2 lb. It was found that when the lobsters were plunged into boiling water 45 minutes' boiling from the time the water again reached boiling-point was usually sufficient, and that the flavour of the lobsters was not thereby impaired. A further experiment was made to ascertain the temperature to which the interior of lobsters is raised by boiling for different lengths of time. The lobsters were taken out, one at a time, the head was broken off, two thermometers were plunged down the neck into the interior of the flesh, and the temperature recorded, the lower reading being taken. The results are given in tabular form as follows:

Number and weight of lobsters	Duration of boiling, minutes	Temp. ° C.
5 (1 lb. 4 oz. each)	10	82·0
	15	84·5
	20	86·6
	25	85·5
	30	89·0
5 (2 lb. each)	25	79·0
	35	91·0
	40	87·5
	47	90·0
	60	91·0

Number and weight of lobsters	Duration of boiling, minutes	Temp. ° C.
11 (2 lb. each)	5	60·0
	10	76·5
	15	76·5
	20	82·0
	25	87·5
	30	82·0
	35	90·5
	40	85·0
	45	90·5
	55	95·5
	75	95·5

It is recommended that the usual time of boiling, *viz.* 25 to 30 minutes, should be extended to 45 minutes for 2-lb. lobsters, and that if there is any doubt how long they have been cooked, it is safer to eat small 1-lb. lobsters or to re-cook larger ones. D. R. W.

Varieties of Yeasts and Bacteria in Fruits. A. Romwalter and A. V. Király. (*Archiv. f. Mikrobiologie*, **1939**, **10**, 87; *J. Inst. Brewing*, **1939**, **45**, 355.)—The isolation of living bacteria from the inner structures of fruit, seeds and plant tissues and from sap is recorded. This raises the question whether methods in common use for the sterilisation of fruit and vegetables are efficient. In the experiments described whole gooseberries were washed with a 0·2 per cent. solution of chlorine and stored for one month. The fleshy portions were found to contain many germinating yeast cells, and carbon dioxide was slowly evolved; an alcoholic odour was also noticeable. In living fruit such fermentation does not occur during ripening and sugar formation. Similar results were obtained with fruit washed in a fairly strong solution of chlorine and subsequently in a 2·5 per cent. solution. Several varieties of yeasts were identified. D. R. W.

Bactericidal Efficiency of certain Aniline Dyes. F. W. Tilley. *J. Agric. Res.*, 1939, 58, 941–946.)—In connection with investigations concerning the hog cholera virus, hog cholera vaccine, stained antigen for the detection of pullorum disease of fowls, and Bang's disease in cattle, the author has carried out a number of tests on the efficiency of aniline dyes as bactericidal agents. The test organisms used were *B. coli*, *B. pullorum*, *B. suipestifer*, *B. typhosum* and *Staphylococcus aureus*, all being Gram-negative except the last. The dyes used were auramine O; the following derivatives of triphenyl methane: basic fuchsin, malachite green, Hofmann's violet, methyl violet, crystal violet, and victoria blue; other dyes, including ethyl green and ethyl violet, thiazine and diazo dyes. The organisms were exposed to the action of these dyes, with and without the addition of phenol, *o*-cresol, sodium carbonate, borax and disodium phosphate, for periods ranging from 5 to 60 minutes. The results of these tests are recorded and may be summarised as follows:—The thiazine and azo dyes were shown to be very ineffective, as was also ethyl violet. Ethyl green (ethylated crystal violet) was tenfold less effective than crystal violet. Basic fuchsin showed comparatively low bactericidal activity. The addition of phenol or ortho-cresol to crystal violet or methyl violet greatly increased their bactericidal activity with Gram-negative bacteria but showed little or no increase with Gram-positive bacteria. The addition of phenol or ortho-cresol to brilliant green or malachite green had little, if any, effect. The addition of sodium carbonate to aqueous solutions of crystal violet increased their bactericidal efficiency to a pronounced extent. The addition of sodium borate or disodium phosphate to such solutions produced little or no effect, but in contaminated hog blood mixtures crystal violet in dilutions of 1000 to 2000 with 0·02 molar disodium phosphate was uniformly effective, with 0·02 molar borax usually effective, and with 0·02 molar sodium carbonate uniformly ineffective.

D. R. W.

Effect of Radiant Energy on Thermophilic Organisms in Sugar. H. H. Hall and J. C. Keane. (*Ind. Eng. Chem.*, 1939, 31, 1168–1170.)—Results obtained in the Bureau of Agricultural Chemistry, U.S.A. Dept. of Agriculture, show that the spores of a thermophilic organism which spoils canned food, *B. stearothermophilus* Donk, are killed in dry white sugar by radiant energy rays, most of which are in the region 253·7$m\mu$, and that enhanced lethal action is obtained when the sugar crystals are kept in constant motion in the sugar granulator. For this purpose, twenty-four 30-inch lamps were installed in the sugar outlet end of a granulator. Under these conditions an average of 47·8 per cent. of the spores were killed by irradiating eight successive batches of sugar. No immediate or delayed physical or chemical changes were noted in the irradiated sugar, and no residual lethal power was retained by the sugar. There was no increase in the spore counts of irradiated samples during storage. The results indicate the possibility of sterilising white sugar and other ingredients of food by irradiation.

Organic

Modified Beilstein Test for Halogens in Organic Compounds. D. F. Hayman. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 470.)—The Beilstein test for halogens in organic compounds often gives results indicating the presence of small amounts, even when halogen is absent, for example, with certain types of pyrimidines, pyridines and oxyquinolines. The following modification, which has been used for five years by the author, has never given a positive test in absence of halogen except with material containing copper. A section of Monel metal tubing, 0·9 cm. in external diameter, is heated to bright redness with a fishtail Bunsen burner, and the compound under examination is brought into the flame on a platinum loop or spoon within 1 cm. of the under side of the tube. In presence of halogen a flare of colour between green and blue is produced. The rate of decomposition, and therefore the type of the colour tint, varies with the compound analysed. With experience, the halogen may be estimated to within 20 per cent. of its actual amount; the method is valuable as a rough quick control of the course of a reaction. E. B. D.

Benzyl-isothio-urea as a Reagent for the Identification of Organic Acids. S. Veibel and K. Ottung. (*Bull. Soc. Chim.*, 1939, **6**, 1434–1435.)—The use of benzyl-isothio-urea hydrochloride, previously suggested as a reagent for the identification of organic acids (Veibel and Lillelund, *Bull. Soc. Chim.*, 1938, **5**, 1153) has been extended to the 15 acids shown in the table, in which some properties of the salts are summarised.

Acid	m.p.	Weight g.	0·098 *N* HCl ml.	Molecular weight		Acid or neutral salt
				calc.	found	
Malic (*d, l*)	159–160	0·0840	7·34	466·4	463·6	neutral
Mucic	194–195	0·2404	17·89	542·4	544·4	
Monochloroacetic	159–160	0·1581	12·24	260·6	261·4	
Dichloroacetic	178–179	0·2565	17·57	295·1	295·8	
Trichloroacetic	148–149	0·1709	10·53	329·5	328·2	
α-Bromopropionic	158–159	0·2367	15·04	319·1	318·4	
Azelaic	163–164	0·1260	9·82	520·4	519·6	
o-Toluic	145–146	0·2151	14·38	302·2	302·6	
p-Hydroxybenzoic	143–145	0·1923	12·84	304·2	303·2	
α-Hydroxynaphthoic	158–159	0·2878	16·40	354·2	355·0	
β-Hydroxynaphthoic	216–217	0·2950	16·90	354·2	353·4	
Phthalic	157–158	0·2007	16·29	498·4	499·2	
Isophthalic	215–216	0·1207	7·32	332·4	334·2	acid
Terephthalic	202–206	0·1244	10·10	498·4	499·2	neutral
Pyromucic	211–212	0·2112	15·40	278·2	277·6	—

It has not been found possible to prepare the salts of the following: glycine, taurine, phenylalanine, tartaric acid, citric acid, and ethylene-tetracarboxylic acid; the salt of isophthalic acid can be isolated only with difficulty. The authors regard their method as better than the similar one proposed by Donleavy (*J. Amer. Chem. Soc.*, 1936, **58**, 1005). E. M. P.

New Method for the Identification of Ethers. P. P. T. Sah. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 758–760.)—Aliphatic ethers can be identified by subjecting them to pyrolysis and identifying the resulting carbonyl compound by some suitable reagent, such as *o*-tolylsemicarbazide (Lei, Sah and Shih, *J. Chinese Chem. Soc.*, 1935, **3**, 246–250), *p*-tolylsemicarbazide (Sah and Lei, *J. Chinese Chem. Soc.*, 1934, **2**, 167–172), *m*-nitrobenzhydrazide (Meng and Sah, *Science Reports, National Tsing Hua University*, 1934, A II, 345; Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 759), or *p*-chlorobenzhydrazide (Shih and Sah, *Science Reports, National Tsing Hua University*, 1934, A II, 353). The procedure is as follows:—One to 2 ml. of the ether is dropped from a dropping funnel into a small distillation flask heated in an oil-bath to a temperature about 20° C. above the b.p. of the ether. The vapour evolved is conducted through a quartz or copper tube heated to 500° C., and the products are passed through a water condenser and collected in a wash-bottle containing 0·2 g. of the reagent dissolved in 10 ml. of 95 per cent. ethyl alcohol, the flask being immersed in a freezing-mixture. The last traces of vapour are collected by the application of mild suction. The contents of the bottle are boiled gently for 10 minutes under reflux in an Erlenmeyer flask. After filtration, the hot filtrate is diluted with an equal volume of water, and the crystalline precipitate, which separates on cooling, is filtered off with the aid of suction and re-crystallised from 50 per cent. or 95 per cent. ethyl alcohol. The melting-points and crystalline forms of the derivatives are determined. With mixed ethers, such as alkyl-benzyl ethers, the pyrolysis products, which contain two hydrocarbons and two carbonyl compounds, are collected in a clean bottle, and the lower-boiling fraction is separated from the benzaldehyde by fractional distillation and identified. The author gives the melting-points of semicarbazones and benzoylhydrazones obtained from the pyrolysis products of 12 ethers.

E. M. P.

Saccharolactone as a Reagent for Precipitating certain Amines. A. C. Kurtz and D. W. Wilson. (*J. Biol. Chem.*, 1939, **129**, 693–699.)—Saccharolactone in conc. alcoholic solution reacts with certain amines at room temperature to give sparingly-soluble *N*, *N*′-substituted saccharamides, which after recrystallisation have sharp, characteristic melting-points that enable them to be readily identified. The following is a list of the amines that gave such well-defined saccharamides, together with their m.p.:—methylamine 188° C., ethylamine 174° C., *n*-propylamine 179° to 181° C., isopropylamine 176° to 178° C., *n*-butylamine 178° C., isobutylamine 159° C., *n*-amylamine 173° to 174° C., isoamylamine 138° C., *n*-heptylamine 174° to 176° C., ethanolamine 129° to 130° C., benzylamine 200° to 201° C., *β*-phenylethylamine 185° to 186° C., tyramine 204° C., and piperidine 191° C. The last-named is the only secondary amine that gave a precipitate. In the series of primary amines tested, the symmetry of the molecule was found to be of great importance in determining precipitability. Thus *n*-butylamine was precipitated immediately, isobutylamine only after 30 minutes, and secondary butylamine not at all; *n*-amylamine and isoamylamine rapidly formed precipitates, whereas 2-methyl-*n*-butylamine did not give a precipitate after several days. The reagent can thus frequently be employed for the separation of amines which otherwise can be separated only with great difficulty. F. A. R.

Antioxidants for Castor Oil. G. O. Inman. (*Ind. Eng. Chem.*, 1939, **31**, 1103–1104.)—It is not uncommon for the acid value of castor oil that has been used as a lubricant to increase in two years by oxidation from 2 to over 35, and for the oil to become green through its action on a brass lubricator. The results of the experiments made to find an inhibitor that would prevent the oxidation of castor oil have confirmed the conclusion of Mattill (*J. Biol. Chem.*, 1931, **90**, 141), that if a phenolic compound contains two hydroxyl groups in the ortho or para position it will have a high antioxygenic action, whilst the corresponding meta isomer will be inactive. Thus hydroquinone and catechol are strong antioxidants, whilst their *m*-isomer, resorcinol, is a weak pro-oxidant. Pyrogallol is a strong antioxidant. All three cresols are mild pro-oxidants, but the *m*-isomer is stronger than the other two. *o*-Nitrophenol is a slightly stronger pro-oxidant than *p*-nitrophenol. Benzyl alcohol is a weaker pro-oxidant than the three cresols.

Inorganic

Determination of Cadmium in Silicate Rocks. E. B. Sandell. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 364–365.)—The method involves differential extraction of metals with carbon tetrachloride in presence of dithizone, and ultimate determination of cadmium colorimetrically with dithizone. It is applicable to traces of cadmium in presence of small amounts of the heavy metals. A 0·5-g. sample of the powdered rock is dissolved, as far as possible, in a platinum dish, in a mixture of 1 ml. of 70 per cent. perchloric acid, 5 ml. of hydrofluoric acid and a little water. The liquid is evaporated to dryness; the residue is successively treated with 0·5 ml. of perchloric acid and then with a little water, with intervening evaporation to dryness, and is finally dissolved, as far as possible, in 6 ml. of 1 : 5 hydrochloric acid. Ten ml. of sodium citrate solution (10 per cent.) and 0·1 g. of hydroxylamine hydrochloride are added, and the solution is rendered slightly ammoniacal. [Main solution.] Any precipitate is filtered off and fused with sodium carbonate, and the extract of the melt is acidified with hydrochloric acid and rendered ammoniacal after addition of a few ml. of the sodium citrate solution and a little hydroxylamine hydrochloride. [Subsidiary solution.] The main solution is extracted by shaking for one minute with successive quantities of 5 ml., or less, of a 0·02 per cent. solution of dithizone in carbon tetrachloride until the carbon tetrachloride layer shows a greenish colour. The subsidiary solution is similarly extracted. The combined dithizone—carbon tetrachloride extracts are washed by shaking with 5 ml. of water, and the solvent layer is then shaken with two successive 5-ml. portions of 0·01 *N* hydrochloric acid. Zinc, lead and cadmium dithizonates are thus decomposed, the metals entering the aqueous phase as chlorides; copper and cobalt remain in the carbon tetrachloride. The aqueous phase is transferred to a stoppered glass colour-comparison tube, and 2·5 ml. of 25 per cent. sodium hydroxide solution are added, followed by 1 ml. of a 0·001 per cent. solution of dithizone in carbon tetrachloride (this weak dithizone should be shaken, before use, with 10 ml. of redistilled water and 2 ml. of 25 per cent. sodium hydroxide solution, in order to free it from colour.) The non-aqueous layer is thoroughly shaken, and, immediately after, its colour is compared with that of standards prepared in a similar manner from, for example, 0, 0·05, 0·1, 0·15γ of cadmium in 0·01 N hydrochloric acid. In test experiments 0·1 per cent. of zinc in the sample gave distinctly less colour than that produced by 0·05γ of cadmium. Nickel interferes if present in more than traces, but tin, bismuth, silver, thallium and manganese in small amounts are without effect. S. G. C.

Colorimetric Determination of Nickel as Nickel-Ammonia Complex Ion. G. H. Ayres and F. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 365–367.)—The transmission of the blue nickel-ammonia complex was measured by means of the Yoe photo-electric colorimeter. This enabled amounts of nickel giving a feeble blue colour, difficult to match by visual inspection, to be estimated. The ammonia concentration should be 1·5 N; larger amounts of ammonia produce violet coloured solutions offering less sensitiveness in determination. Identical transmissions were obtained in ammoniacal solutions prepared from nickel sulphate, nitrate and chloride; ammonium salts had only a slight effect. As little as 5 mg. of nickel per litre can be detected; the highest accuracy is obtainable with 500 to 1500 mg. per litre. The method is, in general, subject to interference by the same ions as affect other colorimetric methods for nickel. Preliminary separation of nickel by precipitation with dimethylglyoxime is advised; the precipitate is decomposed by heating with nitric acid, yielding a solution of nickel nitrate. S. G. C.

Colorimetric Method for the Determination of Rhenium. J. J. Hoffmann and G. E. F. Lundell. (*U.S. Bureau of Standards; Chem. Trade J.*, 1939, Aug. 25, 168.)—A method for the separation and colorimetric determination of rhenium and molybdenum has been based on differential reduction with mercury. When a dilute hydrochloric acid solution of the two metals is shaken with mercury, potassium thiocyanate and ethyl ether, only the molybdenum is reduced to a form that produces an ether-soluble coloured compound with thiocyanate. The colour of the ethereal extract is proportional to the quantity of molybdenum. On adding stannous chloride to the acid solution remaining after the extraction of molybdenum a yellow to yellowish-red ether-soluble compound is produced, and this can be used for the colorimetric determination of rhenium. As little as 0·001 mg. of rhenium can be detected in presence of 10 mg. of molybdenum. Very few elements interfere, and practically all can be eliminated by a simple distillation.

New Indicator for the Argentometric Determination of Chlorides. E. Percs. (*Ber. Ungar. Pharm. Gesellsch.*, 1939, 449; *Pharm. Weekblad*, 1939, **76**, 1238.)—The indicator consists of a saturated solution of trithionine monopicrate in a mixture of methyl alcohol and acetone; this solution is red-violet in colour, but turns blue when the silver salt is produced. For the titration, a solution containing the equivalent of 0·03 g. of chloride is acidified with nitric acid, and 5 ml. of carbon tetrachloride and 8 to 10 drops of the indicator solution are added. The mixture is then titrated with a 0·1 N solution of silver nitrate until the colour of the water layer changes from red-violet to ultramarine. J. G.

Determination of Sulphides by means of Potassium Ferricyanide. G. Charlot. (*Bull. Soc. Chim.*, 1939, **6**, 1447–1451.)—The method depends on the oxidation of soluble sulphides by potassium ferricyanide, with precipitation of sulphur, in a medium buffered to *p*H about 9·4.

(1) *Potentiometric determination.*—The titration is carried out in a tube closed with a 4-bored stopper, the holes carrying a platinum electrode, a calomel electrode, and tubes for the passage of hydrogen through the solution. Into the tube there are introduced 20 ml. of a buffer solution (70 ml. of conc. ammonia and 50 g. of ammonium chloride per litre) and hydrogen is bubbled through for 5 minutes. Ten ml. of the sulphide solution are then added and there is introduced gradually an approximately *N*/10 potassium ferricyanide solution (standardised iodimetrically in presence of a zinc salt by Kolthoff's method, *Z. anal. Chem.*, 1921, **60**, 454), the potential being determined after each addition of the ferricyanide. A curve of the potential in centivolts is plotted against the number of ml. of ferricyanide solution added, and a sharp inflexion point gives the end-point of the titration. The sulphide-content can be calculated from the equation

$$S'' + 2Fe(CN)_6''' \longrightarrow S + 2Fe(CN)_6''''.$$

(2) *Determination by means of ferrous dimethylglyoxime.*—Twenty ml. of the buffer solution are just coloured by adding a few drops of the indicator solution (1 ml. of *N*/50 ferrous sulphate solution, 4 to 5 ml. of saturated alcoholic dimethylglyoxime solution [about 1 per cent.], and 0·5 ml. of conc. ammonia). Air-free hydrogen is passed through for 5 minutes, and the solution to be titrated is then added. The ferricyanide solution is run in, the end-point being the permanent disappearance of the pink colour. To obtain the correct result 0·06 ml. must be subtracted from the volume of ferricyanide solution added, but if the titration is carried out in air, aerial oxidation is sufficient to cancel out this correction. If the sulphide solution is strongly alkaline, sufficient ammonium chloride to react with the free alkali is added.

Determination in presence of sulphite.—Twenty-five ml. of the buffer solution and enough *M*/2 barium chloride solution to precipitate the sulphite are introduced into a flask (50 ml. of barium chloride solution will precipitate completely 10 ml. of saturated sodium sulphite solution). Hydrogen is passed through the liquid for 5 minutes, a few drops of the indicator are added, the mixture is left for 10 minutes for the precipitate to settle, and the liquid is titrated. The determination may be made without any particular precautions in presence of thiosulphates. E. M. P.

Ferrous-Molybdate Reagent for Detection of Small Amounts of Phosphorus, Silicon and Arsenic. J. H. van der Meulen. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 841–846.)—*Reagent.*—Twenty ml. of *M* sodium molybdate solution (242 g. of $Na_2MoO_4.2H_2O$ per litre) are diluted to 900 ml., 40 ml. of acidic *N*/10 ferrous sulphate solution (27·8 g. of $FeSO_4.7H_2O$ per litre of *N* sulphuric acid) are added gradually with shaking, and the whole is diluted to 1 litre. *Use.*—On adding 1 ml. of water containing a small amount of phosphoric acid to 5 ml. of the reagent a greenish colour is produced; the further addition of 0·25 to 0·5 ml.

of alkali fluoride solution produces a deep blue colour; sensitiveness: 0·005 mg. of phosphoric acid. A similar reaction is obtained with arsenic acid, arsenious acid (the formation of the blue colour being rather slower with arsenious acid) and silicic acid, but not with pyrophosphoric acid. The development of a blue colour with silicic acid can be prevented by the addition of fluoride and a little mineral acid to the test solution *before* it is mixed with the reagent.

Silicomolybdic acid reagent for pyrophosphoric acid.—A one-tenth gram-molecular amount of sodium molybdate and a 1/120th gram-molecular amount of sodium silicate are dissolved in 500 ml. of water, 21·7 ml. of 10 *N* sulphuric acid are added, and the mixture is heated on a water-bath until a test sample fails to produce a blue colour with ferrous sulphate solution, after which it is diluted to 1 litre. For use, 0·25 ml. of this reagent is diluted with 10 ml. of water and 0·25 ml. of acidic ferrous sulphate solution (*N*/10, in *N*/10 sulphuric acid) is added. Small amounts of pyrophosphoric acid produce an immediate blue colour, whilst phosphoric, arsenic, arsenious and silicic acids give no colour. S. G. C.

Microchemical

List of Micro-methods for the Determination of Calcium and Phosphate. R. S. Manly. (*Mikrochem.*, 1939, **27**, 145–153.)—A reference list of 27 methods for the determination of calcium and 47 methods for the determination of phosphorus, for less than 1 mg. of the constituent determined, is arranged in order of decreasing quantity of the constituent required. The table is given under the following headings: amount of calcium (or phosphorus) required, constitution of precipitate, principle, special apparatus, special reagents, accuracy or deviation from theory (per cent.), precision or deviation from mean (per cent.), application, comment. J. W. M.

Collected References. Some Micro-methods for the Examination of Beer. G. Ghimicescu (*Mikrochem.*, 1939, **27**, 197–210.)—Methods are summarised for the determination of the following in samples of beer:—carbon dioxide, nitrogen, ammonia, nitrate, ash, alkalinity of ash, dried extract, total acidity, volatile acids, non-volatile acids, lactic acid, glycerol, maltose, dextrose, chloride, sulphate (total, organic and inorganic), phosphate (total, organic and inorganic), boric acid, and total and free sulphurous acid. Twenty-four references are given. J. W. M.

Determination of Anthraquinone-1,8-disulphonic Acid in Presence of other Anthraquinone Sulphonic Acids and Sulphuric Acid. W. Seaman. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 465–469.)—When a mixture of sulphuric acid, anthraquinone-1,8-disulphonic acid (I) and anthraquinone-1, 5-disulphonic acid (II) is treated under standardised conditions with barium chloride solution, the barium salt of (I), which is precipitated, can be readily distinguished from those of the other acids by microscopic examination between Nicol prisms under suitable illumination. It appears as glistening specks or prisms according to the size of the crystals. As the small and large crystals appear to be formed in some constant proportions, a linear relationship may be determined between the count of crystals and the percentage of (I), within certain percentage limits; hence (I) may be determined quantitatively. The method was worked out in detail for mixtures containing 20 per cent. of sulphuric acid, 0 to 20 per cent. of (I) and 80 to 60 per cent. of (II).

The influence of anthraquinone-2,6-disulphonic acid (III), anthraquinone-2, 7-disulphonic acid (IV) and anthraquinone-2-monosulphonic acid (V) on the determination was investigated. The barium salt of (III) forms anisotropic needles, which are counted with (I), but results are not additive; (IV) and (V) may cause low values for (I). It might be possible to determine anthraquinone-1-sulphonic acid in presence of anthraquinone-2-sulphonic acid by a similar method. For the analysis, a percentage/count curve is drawn based on the barium salts of such acids as would be present in the sample analysed, and the percentage corresponding with the count of the sample is calculated from the curve. The original paper gives full details of the preparation of pure reagents and solutions for the plotting of this curve, the precipitation of the salts, and the counting of crystals.

E. B. D.

Micro-determination of Veronal in Blood and Spinal Fluid. R. Fischer. (*Mikrochem.*, 1939, **26**, 255–263.)—At least 2 ml. of blood are mixed with an equal volume of water and treated with an acid buffer solution (1 per cent. sodium phosphate with 0·4 ml. of *m*-phosphoric acid and 0·05 g. of potassium cyanide; *p*H=3·3–3·5) to prevent the separation of proteins, and the veronal is extracted with purified ether. The extract is dried with sodium sulphate, purified with magnesium oxide and charcoal and filtered. The precipitate is washed, and the filtrate is concentrated, evaporated to dryness and sublimed between 90°–150° C. on to a weighed coverslip. The purity of the product is ascertained by microscopic examination before re-weighing the coverslip. The sublimation apparatus used is the author's electrically heated apparatus with an automatic regulator, which combines a melting-point and sublimation block (*Mikrochem.*, 1934, **15**, 247; Abst., ANALYST, 1935, **60**, 123). The limits of error range between 2·5 and 6·7 per cent. for blood and between 2·5 and 4·8 per cent. for spinal fluid, on amounts of veronal ranging from 70 to 300γ. A method is described for the separation of veronal from succinic acid by adsorption on alumina followed by washing with ether containing 20 to 30 per cent. of alcohol.

J. W. M.

Iodimetric Micro-determination of Potassium in Serum. S. Dénes. (*Mikrochem.*, 1939, **26**, 277–281.)—The method gives results that agree with those obtained by Kramer's method to within about 2 per cent. without removal of albumin. A sample of about 0·5 ml. of serum is treated with 1 ml. of Kramer-Tisdall's sodium cobaltinitrite reagent; after 1 hour, 1 ml. of water is added, and the precipitate is centrifuged and washed. It is then taken up in 3 ml. of 0·01 *N* permanganate solution and 0·5 ml. of 20 per cent. sulphuric acid, and the solution is heated for 2 minutes on a water-bath. After cooling, 1 ml. of 10 per cent. potassium iodide solution is added, and the liberated iodine is titrated with 0·01 *N* thiosulphate solution.

J. W. M.

New Test for Thallium. H. Jurány. (*Mikrochem.*, 1939, **27**, 8–13.)—Thallium is precipitated by potassium mercury iodide, $K_2(HgI_4)$, as an orange-yellow crystalline precipitate; under the microscope the crystals appear as yellow rectangles or rods, often grouped together to form crosses or star-shaped clusters. The crystals belong to the tetragonal system with straight extinction, and are optically positive. *Limit of identification*, 0·1γ of thallium; *concentration limit*, 5γ of thallium per ml. Silver, lead, stannous tin and tervalent arsenic interfere with the reaction, but the elements of the ammonium sulphide group, alkaline earths and alkalis do not. During the course of the work three new crystalline compounds formed by $K_2(HgI_4)$ with lead ions, with caesium chloride, and with a mixture of the chlorides of caesium and rubidium were discovered; a brief description is given of these. J. W. M.

Physical Methods, Apparatus, etc.

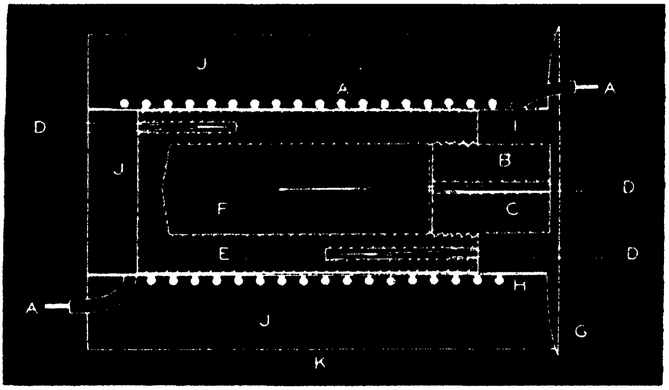
Quantitative Spectrographic Analysis of Solder, Spelter, and Magnesium and Aluminium Alloys. J. A. C. McClelland and H. K. Whalley. (*Spectrochimica Acta*, 1939, **1**, 21.)—The spectra of the samples are excited by the spark method, a circuit with a condenser of 0·005μF, and an inductance of 0·125 or 0·25*m*H being used. A special jig is described for accurate setting up of the electrodes. The spectrograms are examined with a photometric apparatus incorporating a photo-electric cell. The determinations are made by the use of modifications of Gerlach's internal standard method. The authors describe two methods, *viz.* the variant and the constant exposure method. Details are given of the general procedure to be adopted in carrying out either of these two methods, but no analytical tables are given for any of the specific impurities that are being determined. A study is made of the accuracy and reproducibility of the methods, and it is concluded that extensive use in routine work indicates that an accuracy within ±5 per cent. of the amount of the constituent determined may justifiably be claimed. The following details of technique are found to be of importance. (*a*) In every instance the standards are chosen from alloys of composition similar in all respects to the samples to be analysed. (*b*) A preliminary period of sparking is given to free the surface of the electrodes from incidental impurities, and to bring the surfaces into a steady sparking condition. By this means the initial variation of the relative line intensities in the spectrum caused by preferential volatility and oxidation of certain constituents is minimised. (*c*) Variation of electrode size is found to be much less important in those instances in which the minor constituents have no marked preferential volatility. A tabular summary is given of the alloys examined; this includes a list of the impurities determined, circuit details, exposure times and the lines used as internal standards (*cf.* *J. Soc. Chem. Ind.*, 1937, **56**, 177T, 438T.) B. S. C.

Longitudinal Scattering of Light (Plotnikow Effect) and its Importance in Biology. M. E. Jörg. (*Fundamenta Radiologica*, 1939, **4**, 9–17.)—The nature of the Plotnikow effect is outlined (*cf.* Mitchell, ANALYST, 1935, **60**, 454).

The magnitude of the effect depends on, and may be used to indicate the nature of, the molecular state of the substance producing it, and details are given of two applications of this nature, in which the scattering of ultra-violet, violet, blue, green and infra-red radiations (wave-lengths, 318, 375 to 400, 450, 519 to 590 and 740 to 1000$m\mu$, respectively) were measured. The necessary radiations were isolated by means of filters in the usual way, the source for all except the ultra-violet rays being a cinematograph arc-lamp (100 volts, 40 amps.), provided with impregnated carbons and a water-cooled housing. A diaphragm and an aplanatic microscope condenser (aperture, 1·4) were used to obtain an intense parallel beam of light, and this was directed on to a 10- or 20-cm. layer of the solution to be tested, which was contained in a glass cell with plane parallel walls. The usual type of Plotnikow screening-tube was used for obtaining the scattered light (*cf.* Mitchell, *loc. cit.*) and a Wratten filter (No. 87) served to isolate the infra-red radiations used for this purpose. The aurora produced by the scattering was photographed on a Kodak panchromatic plate, which was developed with pyrogallol (6 minutes at 17° C.), and fixed and washed in the usual way. The apparatus was tested with hexane (which has no scattering capacity), and under these conditions no aurora was produced after an exposure of 90 minutes, although some slight trouble was experienced from the Foucault-lens effect of the walls of the containing-vessel. The diameters of the aurora were measured by means of a photo-electric scanning device, the electrical impulses from which were translated (through the medium of the oscillations of a galvanometer-mirror and a revolving drum carrying a light-sensitive paper) into a continuous record. Curves relating the diameters of the aurora and the wave-lengths of the exciting radiations could then be drawn. Water taken from the surface of the Sargasso sea was tested (1) after filtration through filter-paper, (2) after four subsequent ultra-filtrations through a Bechhold collodion-cellulose acetate filter, (3) after boiling followed by a fifth ultra-filtration, and (4) after distillation. After the first ultra-filtration 0·4 per cent. of organic matter was present, but none was detectable after the fifth ultra-filtration. The results indicated a considerable scattering capacity after simple filtration throughout the whole spectral range, but especially with ultra-violet rays. After the first ultra-filtration the scattering was less, especially for the ultra-violet rays, and the three following ultra-filtrations resulted in further rapid decreases, except for the infra-red range; the diameters of the aurora falling in this instance only from 15·32 to 15·20 mm. After boiling and the fifth ultra-filtration the scattering of the infra-red rays was reduced to 15·18 mm., and, except for a slight scattering of green rays (8·2 mm.), no Plotnikow effect was apparent with the other regions of the spectrum tested. After distillation there remained only a slight scattering (9·5 mm.) of the infra-red rays. Photographs of the corresponding aurora are reproduced in the paper. When dust-free water was distilled three times in a vacuum, a similar result was obtained (*i.e.* a scattering of diameter 8·18 mm. in the infra-red region only, which is known as the "limiting dispersion"). The results indicate that the characteristic colour, viscosity and physical properties of the Sargasso sea-water are due to organic substances of high molecular weights, which cannot be removed completely by successive ultra-filtrations. Similar experiments were made with a synthetic resin, prepared from urea, glycerin and an aliphatic aldehyde, in the fluid, viscous and solid states. In none of these was there scattering of the ultra-violet, violet or blue rays; scattering of the green rays was very weak, 9·23 mm., and very weak for the three states, respectively, whilst the scattering of infra-red rays corresponded with auroras of diameters 9·2, 12·3 and 9·2 mm., respectively. These results confirm the view that in the first stage, when the resin is fluid and optically-clear, long-chain molecules have only started to form by polymerisation, and that this process is completed in the second stage; the third (*i.e.* hardening) stage corresponds with the formation of cyclic compounds from these molecular chains (*cf.* following abstract). J. G.

New Optical Method for the Measurement of the Rate of Coagulation of Blood. P. Gjurić and J. Plotnikow. (*Fundamenta Radiologica*, 1939, **4**, 92–95.)—The longitudinal scattering of light (the Plotnikow effect, *cf.* preceding abstract) of blood plasma increases with the lapse of time to a limiting value, at a rate which can be measured by photo-electric methods (*loc. cit.*). The curve relating the Plotnikow effect and the time may therefore be used to follow the course of the coagulation of blood. In an explanatory note Plotnikow points out how the method may be used to follow other processes involving polymerisation reactions; to establish whether these reactions are mono- or bimolecular in type; also to measure their reaction-velocities and the effects on them of temperature, catalysts, etc. The difference in this respect between long-chain macro-molecules and suspended particles, and the difficulties of interpreting results obtained with mixtures of these, are also pointed out (*cf.* preceding abstract); the macro-molecules may give a clear solution (as with blood plasma and certain synthetic resins), and yet produce a marked Plotnikow effect, especially towards infra-red radiation. Similarly, the effect is characteristic of highly-viscous substances, whether organic or inorganic, but it is not as yet possible to deduce an exact and generalised correlation between the magnitude of the effect and the structure of the substance producing it; this applies particularly to short-chain molecules. With molecules in which the chain structure is particularly long the scattered light may itself undergo a "bending" effect (known as "scattering reflection"), and when such light strikes a substance having a different degree of opacity or scattering capacity as compared with its surroundings, it is possible to produce an image of the substance in question on a photographic plate (*cf.* L. Freund, *id.*, 1938, **2**, 100). An example of an application of this modification of the method is given by M. Jörg (*Photog. Korresp.*, 1938, **74**, Sept.); it refers to a hunt for a man with star-shaped tattoo mark. This mark had been rendered invisible to the eye and to the usual methods of detection (*e.g.* photography with a panchromatic plate) by the browning effect produced by exposure to ultra-violet light. The actual tattoo mark, however, was still in existence under the skin, and the method outlined above enabled it to be detected. Other applications are indicated. J. G.

Exothermal Decomposition Temperature of Wood. K. A. Kobe and F. L. Goin. (*Ind. Eng. Chem.*, 1939, **31**, 1171–1172.)—An apparatus has been devised to determine the effect on the exothermal decomposition temperature of wood caused by impregnating it with inflammable organic solvents such as gasoline kerosene, light and heavy motor oils and creosote. In a recent legal case the point was made that wood so impregnated had a much lower exothermal decomposition point than untreated wood. In the procedure described the lowest temperature at which the temperature of the wood will rise above the retort temperature, when heated in absence of air, is termed the "exothermic point." The retort, E, used, consisted of steel shafting (2 in. × 5 in.) in which a hole, F (1 in. × 4½ in.), was drilled. The outer end of the hole was threaded to take a plug in which was drilled an opening for a thermo-couple. The lower and upper portions of this hole were filled with steel, a rectangular opening (1 in. × ⅜ in.) being left, into which the test specimen of spruce wood was fitted tightly. The retort was fitted closely into a metal sleeve, H, which was covered with mica and wound with resistance wire to form a heating element, A. This was placed inside a can, K, and insulated with magnesia, J, except at the outer end, where the can cover, G, left a dead air space, I. More resistance wire at this end of the heating element gave a uniform temperature along the retort. The temperature of the wall was measured in two places by means of thermo-couples, D, and the temperature of the wood was measured with another thermo-couple placed in the centre of the test specimen. The heating rate was controlled by variable resistances in series with the heating element. The retort was heated rapidly to about 250° C., and maintained at that temperature until the wood temperature was within 20° C. of the wall temperature. The rheostats were then adjusted until a rise of 2° C. in the temperature of the retort wall was recorded. Readings were taken every minute on each of the three thermo-couples. In the first few minutes of the test the temperature of the wood rose above that of the retort wall, increased at the same rate as the wall temperature, and then began to fall to the temperature of the wall. The temperatures of wall and wood were plotted against time, and the point of intersection of the two curves was taken as the exothermal decomposition temperature. The following results were thus obtained with spruce; the impregnated specimens showed uniform staining with the liquid when cut in half.



Treatment of sample	Weight before treatment g.	Weight after treatment g.	Gain Per Cent.	Weight after charring g.	Loss Per Cent.	Temperature of decomposition ° C.
As received ..	4·538	—	—	3·348	26	273
Oven-dried ..	4·945	4·545	−8·1	3·535	29	276
Dioxane	4·456	5·325	19	2·350	47	275
Gasoline	4·215	4·587	8·1	1·955	54	363
Kerosene	5·044	6·262	24	3·875	23	266
Light motor oil ..	4·198	5·935	41	2·900	31	267
Heavy motor oil ..	4·542	7·065	56	3·779	20	272
Creosote	4·430	6·765	52	2·965	33	284

Moisture had no appreciable effect on the result, for the oven-dried sample decomposed within 3° C. of the sample containing 10 per cent. of moisture. Removal of moisture with dioxane and impregnation of the wood with that substance, itself containing 36 per cent. of oxygen, had no effect on the exothermal point. Volatile liquids, such as gasoline and kerosene, lowered the exothermal point, which, however, increased with the b.p. of the liquid. Creosote increased the exothermal point.

Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Fourth Edition. By Sir J. F. THORPE, C.B.E., D.Sc., F.R.S., and M. A. WHITELEY, O.B.E., D.Sc., F.I.C. Vol. III. Pp. 608. London: Longmans, Green & Co. Price 63s.

This volume starts with chemical calculations and chemical warfare, includes long major articles on cyanides, chlorine, crystallisation, corrosion, deuterium and diazo compounds, and ends with one on diffusion. It provides a truly remarkable amount of information on these and a wide range of other topics, some of which have not appeared in earlier editions. The editors have most delightfully disarmed all reviewers and critics by their very apt Foreword taken from Dr. Samuel Johnson's preface to his famous Dictionary in 1755. The great doctor counted himself among the unhappy mortals who write dictionaries, but by his work he joined the immortals; if Sir Jocelyn Thorpe and Dr. Whiteley have not yet attained to that felicity they have at least assured for their names a lasting place in the annals of industrial chemistry by producing a dictionary which to chemists is as essential as ever Johnson's was to savants of his time.

Chemical calculations are well known in some circles, but little valued, even shunned, in others; hence it is useful to have a selection of time-saving methods of much practical value simply explained. Chemical warfare and its defence, over the familiar initials J.D.P., is of such obvious interest that no commendation is needed. The articles on chlorine and on cyanides have been largely rewritten by F. Holt and G. E. Wainwright, respectively; both are concerned with fundamental products of greatly increased importance in our industry, and these have been the subject of many patents and new processes, all the most important of which are skilfully summarised.

Colorimeters and comparators form the subject of a well-written monograph by

J. Guild; it is of much interest to the analyst in view of the increasing applications of colorimetric methods in various branches of our work. Then, as a chemical antidote to any who may think they have had an overdose of physics, one may turn to an account of colour and chemical constitution—a subject that has gone out of fashion of late—and a brief but comprehensive survey of co-ordination compounds by G.T.M. and F.H.B.

Cryoscopy is perhaps among the articles to which many analysts will turn. In addition to the familiar Beckmann apparatus, it describes the more elegant micro and semi-micro methods of Rast, which deserve to be more widely used; some of us would have liked to see mention of Hortvet's method, as that, too, can be applied to many things besides milk.

Mention may be made of the up-to-date monograph on Deuterium if only because its study is now being so actively pursued and because it affords so useful an indicator to the course of organic reactions and of biological metabolism. But it is hopeless to attempt to comment on even the major articles, for there are about 250 which may be so described. The reviewer has pored over the new volume, tested it on such subjects as he was able to, and consulted it on the day-to-day problems of the practising chemist. He finds it full of valuable information, for few of the articles can be read without learning something hitherto unknown or unrealised. It is singularly free from misprints and enhances the traditions of its predecessors. Thorpe's Dictionary is a necessity on our book-shelves, and we are indebted to its authors, contributors and publishers for keeping it so thoroughly up-to-date and authoritative.

H. E. Cox

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Editor-in-Chief, JOHN R. JOHNSON. Pp. 105. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1939. Price 8s. 6d. net.

The nineteenth volume of this well-known series has now been issued. It is, in arrangement and appearance, identical with its predecessors. Details of thirty preparations are given together with some additions and corrections for preceding volumes. An index for Volumes X–XIX inclusive is also provided.

Many of the preparations involve either cyclic or heterocyclic compounds, and some of the reactions afford good examples of ring closure or rupture. Among the more noteworthy preparations may be mentioned that of the useful reagent phenacyl bromide, the hydroaromatic-aromatic compound phenyl cyclohexane, and *para*-dinitrobenzene, the preparation of which gives an interesting use of hydroborofluoric acid in the replacement of the amino group by the nitro group. Some interesting iodo compounds are also dealt with.

In conclusion, it may be stated without reserve, that Volume XIX of Organic Syntheses is a worthy member of this series.

HAROLD TOMS

SOIL ANALYSIS. By C. HAROLD WRIGHT, M.A., F.I.C. Pp. x + 276. Second Edition. London: Thomas Murby & Co. Price 12s. 6d. net.

Five years ago the first edition of "Soil Analysis" was published, and the comparatively early appearance of the second edition denotes that analysts have found the former work to be valuable. The work has only been extended by forty pages, but these additional pages do not represent all the new matter incorporated, because some methods have been omitted and the space occupied by processes now considered to have a greater value or to have wider application.

Mr. Wright has had the assistance of a considerable number of acknowledged experts in the production of this work, and, therefore, its revision before publication has been placed before highly qualified analysts, many of whom devote a considerable portion of their time to soil study.

The first revision noted is that of the chapter dealing with the mechanical analysis of soils, and the author has here had the assistance of Dr. G. W. Robinson. The methods of dispersion agreed to internationally at Versailles in 1934, and at Leningrad in 1930, are given in detail, and these are now of considerable importance. The section on hydrogen ion concentration has largely been reproduced, but the quinhydrone electrode has been more clearly and carefully explained, and articles on glass and antimony electrodes have been added. Methods for the determination of various metals occurring in soils are given and, as alteration of details in a number of instances has been made, enquiry has undoubtedly taken place since the appearance of the first edition. From the description of processes involving the use of cobaltinitrite for the determination of potassium both gravimetrically and volumetrically, it would appear that the author favours one or the other of these as a method to be employed. However, throughout the book, although he has had considerable experience in the examination of soils, he invariably refrains from suggesting which of the processes given should be used for a determination, but he does usually indicate the advantage that one method may have over another.

The original section of the book which dealt with the very important processes for the determination of nitrogen in its various forms of combination, was, in my opinion, too short for it to give an analyst even an insight into the varied methods applicable. This part of the book has now been extended and the subject given the attention that it deserves.

We are apt to forget that for a process to be of use to the practical man the results obtained by it must have a practical interpretation. The results given by some old processes may not attain to high scientific accuracy, but they were capable of translation, so that the best agricultural procedure was indicated. In this connection it was with a little concern that it was noted that one old, but largely used and valued, process for the estimation of lime requirement of soils was not even mentioned in the present book. Possibly the author is correct in limiting his outlook generally to processes complying with modern scientific outlook, but, even though there may be much to recommend these processes, it may need some years of experiment before the laboratory results can be correlated with farm results.

The first edition I welcomed, as it brought together so much scattered information, and I hold the same view now. The serviceability and utility of the second edition is unquestioned.

F. W. F. ARNAUD

THE CHEMICAL FORMULARY. Vol. IV. Editor-in-Chief, H. BENNETT. Pp. 632. London: Chapman & Hall, Ltd. 1939. Price 25s. net.

The previous volumes of this publication were issued between 1934 and 1936, and the contents of these, together with those of the present one, have been submitted to a board of editors, the members of which are engaged in educational or industrial work. Thus the text, which comprises several thousands of formulae for preparations applicable to a wide range of uses, together with the methods used in compounding them, may be relied upon as practical and trustworthy.

A lengthy introduction provides much sound information on the general principles involved in the methods used in compounding preparations of all kinds, together with a series of varied recipes for easily prepared mixtures. The next and principal portion of the volume is devoted to a miscellaneous collection of formulae arranged under some twenty headings covering a very extensive field. Most of the preparations given are of recent origin, since many of the components have been available only during the last few years whilst other formulae are derived from European, Canadian and American patents. In the preface the editor states that, in addition to the usual purposes of these volumes, they may serve to make chemistry useful and interesting to students by teaching them to prepare adhesives, insecticides, etc., but surely the sections devoted to pyrotechnics and explosives would prove far more attractive to the majority of pupils.

It would appear that the American definition of the term "Cosmetic" is very different from that adopted in this country, since under this heading we find such diverse matters as moth balls, lavatory deodorants and tobacco pipe cleaners. As many of the substances included in the various formulae are given their trade names, an extensive list of firms supplying these, both in the United States and elsewhere, is given at the end of the volume, and this is followed by a comprehensive and accurate index in which, however, more cross-indexing would have been advantageous. There are a few typographical errors, but these are of minor importance. The volume is a valuable and up-to-date compilation which will prove of service in many domestic and industrial activities and will, in addition, indicate to the chemist substances for which search should be made when analysing a preparation outside the range of his usual practice.

T. J. WARD

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

The following candidates have been elected members of the Society:

- Frank Wynn Hayes, Chemist in the South African Sugar Industry.
- Geoffrey William Peter Stretton, B.Sc. (Lond.), A.I.C., Chief Assistant to Messrs. Colwell and Lickorish, Public Analysts and Consultants.
- Ernest Victor Suckling, M.B., B.S. (Lond.), M.R.C.S. (Eng.), L.R.C.P. (Lond.), D.P.H. (Lond.), Bacteriologist and Water Analyst to the Essex County Council, and Consultant.
- Donald Frederick Withers, B.Sc., A.I.C., Analyst with the Mond Nickel Company, Limited.

The Determination of Paraldehyde

By D. J. T. BAGNALL, A.C.G.F.C., F.I.C., A. SMITH, B.Sc., F.I.C.,
AND A. R. TANKARD, F.I.C.

(*Read at the Meeting of the North of England Section, March* 25, 1939)

The tri-molecular form of acetaldehyde, known as paraldehyde, $(CH_3.CHO)_3$, is an internal ether, and is a colourless neutral liquid of characteristic ethereal odour, reminiscent of ethyl nitrite. The paraldehyde of the British Pharmacopoeia has sp.gr. 0·998 to 1·000, melts at about 11° C., and has a boiling-range of 123° to 126° C. It is extensively used in medicine as a sedative and hypnotic agent, and closely resembles chloral hydrate in its pharmacological action. Fatal cases of poisoning from the ingestion of one to four fluid ounces of paraldehyde have been recorded, but recovery has occurred after the taking of 3½ fluid ounces.

Paraldehyde is rapidly absorbed in the system and exerts a diuretic action, being excreted mainly by the kidneys and partly by the lungs. Although it is generally considered to be a relatively safe sedative, the opinion[1] has been expressed that paraldehyde is more dangerous than many of the drugs in the fourth schedule of the Poisons List. Idiosyncrasy to the action of the drug has been noted and, in cases of addiction, tolerance is exhibited, and an increase in dosage may be required to produce the desired effect. In some cases paraldehyde is stated to have an irritant action on the lungs and intestinal canal.

Medicinal paraldehyde is usually a mixture of various polymerides of acetaldehyde, together with impurities, such as metaldehyde, $(CH_3.CHO)_x$, which is poisonous and has been stated to be invariably present in traces in paraldehyde. Diacetyl peroxide, acetic acid and acetaldehyde are also usually present, but the amounts are restricted by the limit tests of the British Pharmacopoeia. Other possible impurities are acetal, mineral acids, ethyl alcohol, crotonaldehyde, valeraldehyde, valeric acid, amyl alcohol, etc. For the analytical examination of paraldehyde, Craven[2] adopts the following methods:

CRAVEN'S PROCEDURE.—Metaldehyde is determined approximately by weighing the residue from the evaporation of the paraldehyde *in vacuo* at room temperature, allowance being made for any inorganic impurities present.

Acetaldehyde is determined by the hydroxylamine hydrochloride method of the British Pharmacopoeia, bromophenol blue being used as indicator; or by the employment of hydroxylamine sulphate in aqueous solution, with methyl orange or methyl orange and xylene-cyanol as indicator. The titration should be rapidly carried to the neutral point. Ripper's[3] bisulphite method may also be employed, since paraldehyde is not affected.

In absence of water and other impurities the amount of acetaldehyde present in paraldehyde, up to a maximum of 20 per cent., may be deduced from the specific gravity; percentage weight of acetaldehyde $= \dfrac{1{\cdot}0008 - \text{sp.gr.}}{0{\cdot}00237}$

According to Craven, the effects of acetaldehyde and of acetic acid on the m.p. of paraldehyde are as follows:

Acetaldehyde, per cent., by weight	0	2	4	6	8	10	12	14	16	18	20
Melting-point, °C.	12·5	10·1	7·6	5·3	3·0	1·0	−0·9	−2·7	−4·6	−6·4	−8·2
Acetic acid, per cent., by weight	0	2	4	6	8	10	12	14	16	18	
Melting-point, °C.	12·5	11·35	10·2	9·0	7·8	6·6	5·4	4·2	2·95	1·75	

Allowance having been made for these impurities, any excess depression of the melting-point is due to water, each one per cent. of which causes a depression of 3·9° C.

The pharmacopoeial methods are used for the detection of acetic and other acids, etc.

Diacetyl peroxide is determined by treating 1 ml. or more of the sample in a 100-ml. stoppered flask (from which air has been displaced by carbon dioxide) with 10 ml. of 0·5 *N* potassium iodide solution and 5 ml. of dilute (1:1) sulphuric acid. The mixture is heated to 60° C. for 15 minutes and cooled, 100 ml. of distilled water are added, and the freed iodine is titrated with 0·1 *N* thiosulphate solution. One ml. of thiosulphate ≡ 0·0059 g. of diacetyl peroxide.

Orton and McKie[4] have described a method for determining the amounts of acetaldehyde, acetal and paraldehyde in admixture. It depends on the selective decomposition of acetal and paraldehyde by acids. For the determination o acetal, 0·2 to 0·4 g. of the mixture is added to 7 ml. of 0·01 *N* acetic acid diluted with 23 ml. of water. This acid solution is distilled by gentle heating, an efficient condenser being used, and 7 ml. of distillate are received in a small measuring cylinder (kept well cooled and containing 10 ml. of water or alcohol) attached to the condenser by an adapter. For the determination of paraldehyde (or total paraldehyde + acetal), 30 ml. of 0·2 *N* hydrochloric acid are used, and 10 ml. should be distilled from the acid mixture. Under these conditions paraldehyde is wholly converted into acetaldehyde, and acetal is hydrolysed into alcohol and acetaldehyde. The acetaldehyde is determined in the distillates by Ripper's modification of the hydrogen sulphite process or by Seyewetz's neutral sulphite process. Paraldehyde does not react with sulphites. Thus by determining (*a*) acetaldehyde, (*b*) acetaldehyde and acetal, and (*c*) acetaldehyde, acetal and paraldehyde, the proportions of each of these substances in any mixture can be found.

DETECTION OF PARALDEHYDE.—The characteristic odour of paraldehyde, together with the production of acetaldehyde on warming an acidified solution, and the reduction by this solution of an ammoniacal solution of silver nitrate with the formation of a silver mirror, will suffice for the identification of paraldehyde.* Paraldehyde will often come over as oily drops on distillation of an aqueous solution containing it; it may then be separated and its physical constants determined.

DETERMINATION OF PARALDEHYDE.—The methods that have been proposed for the determination of paraldehyde are based on its depolymerisation into acetaldehyde, and a determination of this aldehyde by well-known reactions. We find that when purified paraldehyde is heated at 100° C. in a pressure bottle with hydrogen peroxide and a known amount of sulphuric acid, and the acetic acid formed is titrated (account being taken of the added sulphuric acid), a result equal to about 94 per cent. of the theoretical amount is obtained. When hydroxylamine hydrochloride is substituted for the hydrogen peroxide, the result is equivalent to about 96 per cent. of the paraldehyde taken. Methods in which potassium dichromate in acid solution is used as the oxidising agent, and in which after addition of potassium iodide the liberated iodine is titrated, are less satisfactory.

Craven[5] has described the use of Agulhon's reagent for the colorimetric determination of various alcohols and aldehydes.[6] Contrary to the statement of other workers,[7] Craven finds that Agulhon's solution reacts also with polymerised aldehydes, such as paraldehyde, etc. He employs a 0·1 *N* solution of dichromate (4·9 g. per litre) in nitric acid of sp.gr. 1·31. This acid is prepared by mixing 3 vols. of conc. nitric acid with 1 vol. of water and completely freeing the solution from nitrous vapours by air-blowing. The precise strength of the nitric acid used appears to be of little importance. The depth of the blue colour produced in the reaction, which is given by all primary and secondary alcohols, saccharides, formaldehyde, various acetals and esters, in addition to polymeric aldehydes, is compared with that given by a standard solution of the substance to be determined. This process has been successfully used for the determination of alcohol and aldehyde in acetone. Craven (*loc. cit.*[6]) states that, in the absence of oxidisable impurities, or if a correction be made for any acetaldehyde present, the Agulhon method will give an approximate determination (within 2 per cent.) of the paraldehyde present in the medicinal preparation, and we have found the method to be quite satisfactory within the limits specified. The fact that alcohol gives the reaction renders this method of limited use for the determination of paraldehyde in material from poisoning cases, when alcohol may be simultaneously present with paraldehyde.

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* The British Pharmacopoeia states that a silver mirror is produced when a saturated aqueous solution of paraldehyde is warmed with ammoniacal silver nitrate solution. This reaction does not take place with pure paraldehyde, any reduction being due to impurities such as acetaldehyde, etc.

PROCEDURE IN POISONING CASES.—We recommend the following procedure for the determination of paraldehyde in poisoning cases. The method is based on the formation of acetaldehyde which, when distilled into hydroxylamine hydrochloride solution, forms an oxime and liberates hydrochloric acid. The acid produced is titrated with standard alkali.[8] If viscera or similar material are to be examined they should first be minced, preferably in a frozen state. Freezing facilitates the process of division and minimises loss of paraldehyde. About 50 g. of the material are placed in a flask of one litre capacity, and 100 ml. of a mixture of equal volumes of alcohol and water are added, together with 1 to 2 ml. of concentrated sulphuric acid. The flask is at once fitted to a (Young's 20-disc) fractionating column and an efficient condenser, the end of which is connected with a large bulbed delivery tube which dips into a 5 per cent. alcoholic solution (50 per cent. alcohol) of neutralised hydroxylamine hydrochloride. The volume of hydroxylamine hydrochloride solution employed depends upon the amount of paraldehyde present; with 0·20 g. of the aldehyde, about 10 ml. of the hydroxylamine hydrochloride solution are required. This solution is prepared by adding 2 or 3 drops of bromophenol blue indicator (B.P. solution) to 20 ml. of the solution of hydroxylamine hydrochloride, and neutralising it with sodium hydroxide to a green end-point. The neutralised solution is divided into two equal parts, and one half is reserved as a colour standard for the end-point of the titration. The material in the distillation-flask is gently warmed for a few minutes, and then steam-distilled, very slowly in the initial stages, to prevent any unchanged paraldehyde coming over. When at least 100 ml. have been collected, the distillate is titrated with 0·1 N sodium hydroxide solution to the standard end-point. The distillation is continued into the titrated hydroxylamine hydrochloride solution, and is considered complete if no change of colour occurs when a further 50 ml. of distillate have been collected. If the distillate is acid, it is again brought to the standard end-point. 1 ml. of 0·1 N NaOH $\equiv$ 0·0044 g. of paraldehyde.

A blank test is carried out in the same way, to obtain the correction for any volatile acids and aldehydes in the alcohol. The reserved portion of the neutralised hydroxylamine hydrochloride solution is used for this purpose, and the titration is taken to the same end-point as in the main distillation. Alternatively, purified alcohol, free from these impurities, may be employed.[9] Since stomach-contents, viscera, etc., will usually contain small amounts of volatile acids which should be allowed for, these must be determined on a separate quantity by distillation, in presence of sulphuric acid, into standard sodium hydroxide solution, bromophenol blue again being used as indicator and the distillate titrated back to the standard end-point.

The following results were obtained by this method:

Paraldehyde taken g.	Paraldehyde found g.	Percentage of paraldehyde recovered
0·200; 0·200 } in aqueous solution	0·192; 0·192	96·0; 96·0
0·247; 0·247 } in aqueous solution	2·237; 0·236	96·0; 95·5
0·201 (in presence of minced liver)	0·184	91·5
0·201 (in artificial stomach-contents)	0·186	92·5

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April, 1939

Counterfeit Coins

BY A. SCOTT-DODD, B.SC., PH.D., F.I.C., F.R.S.E.

(*Read at the Meeting of the Scottish Section, April* 28, 1939)

COINING offences are not nearly so common in this country as in some other parts of the British Empire. It is, therefore, only at somewhat rare intervals that Public Analysts here are called upon to investigate falsifications of this nature.

Several references to counterfeit coins have been published from time to time. These are mainly from sources outside the British Isles and relate as a rule to silver coins. A description of a counterfeit gold coin uttered in Trinidad is, however, given by Shrewsbury.[1] It was found to consist of 91·5 per cent. of platinum together with some antimony and copper. It is noteworthy that gilded platinum appears to have been the metal employed on several occasions for making counterfeit sovereigns. Some of these were dated 1862 and 1863. It is to be presumed that at the time of the production of the counterfeit coins platinum was cheap enough to give the counterfeiters a fair margin of profit.

Coining has always been an offence against the realm and punishable as a felony. Severe penalties were enforced on offenders in early days under the West Saxon kings, and, up to the time of Henry I, lopping off the right hand was one of the mildest of mutilations inflicted on coiners; boiling alive was a common punishment. The laws against coining were codified in 1861, and supplemented by the Counterfeit Medals Act of 1883. By these laws offences are punishable by terms of imprisonment ranging from penal servitude for life to two years' imprisonment with or without hard labour. At the present time coining offences are usually charged under the Coinage Offences Act, 1936.

TYPES OF COUNTERFEIT COINS.—Counterfeit coins are of two kinds: those cast or made in moulds, and those struck by means of dies. The coins are usually made of some metal or alloy of colour similar to that of the coin which it is meant to represent, but occasionally the counterfeit coins, after being cast, are coated with silver or gold to render the fraud less obvious. The moulds employed are usually made of plaster of Paris, clay, moulding sand or sometimes copper. The plaster of Paris moulds are made by pressing a genuine coin between two interlocking slabs of unset plaster of Paris. A channel is left at one end between the slabs to admit the molten metal, which is then allowed to cool, after which the moulds are opened to allow the moulded coin to fall out. Coins made in this way have a "runner" or "tail" of metal at the edge where the metal was poured in. This "runner" is removed with a file, and the milling is reconstructed as skilfully as possible. This frequently leaves an imperfection in the milling, which gives a clue to the coin being counterfeit.

A large proportion of the counterfeit coins made in Egypt are struck and many are excellent imitations. To make struck coins at least two separate operations are required: first the punching of circular pieces of metal of the correct size and weight from a sheet or strip, and secondly impressing on these "blanks" the design of the coin. This impression is made from dies by means of a press. Recourse has been had to various devices for producing the milling. The dies are made of steel, and much skill is required for their preparation.

PHYSICAL CHARACTERISTICS.—Struck coins are often very well executed and are therefore very difficult to detect, especially if the composition of the material used closely resembles that of genuine coins. Worn counterfeit coins are even more difficult to identify than new ones. The most important points which the analyst has to examine are the details of the design, quality of workmanship and milling. The milling on a genuine coin is regular and at right angles to the face of the coin, whereas that of counterfeit coins is often irregular and slanting. In cast coins there is sometimes a fault down the centre of the milling where the halves of the mould came together. The number of ridges which constitute the milling can best be counted by colouring the edge with an aniline inking-pad and then making an impression of it. This should be compared with a genuine coin.

The weight and specific gravity of suspected coins are useful indications. Any marked excess in weight is certain proof that the coin is not genuine, but, on the other hand, a distinct deficiency may be due only to the coin being worn. Hardness sometimes affords a useful clue, as also does the "ring" when the coin is dropped on a hard surface. Any marked peculiarity in colour, whether yellowish or leaden, may give an indication that a coin is counterfeit. Similarity in flaws found on counterfeit coins affords information as to the identity of their source of manufacture. For presentation in Court it is often useful to have either photographic enlargements or rubbings of the coins. These are especially helpful when there are any distinct imperfections on the surface of the coin.

The chemist is frequently asked about the various apparatus and appliances used in making counterfeit coins, such as crucibles, moulds, etc. Much ingenuity is sometimes displayed in adapting primitive appliances intended for other purposes to the needs of the coiner. It is necessary to note the shape of the moulds and to identify the metal found on them so as to show the possibility of their having been employed to make coins similar to those found. The same remark applies to the various appliances which may contain quantities of metal, the composition of which would show its association with the alleged counterfeiting.

COMPOSITION.—A qualitative analysis of counterfeit coins is nearly always required. A quantitative analysis is frequently useful when it is necessary to compare it with metal found on the premises of the accused. A historical survey of the coinage of this country reveals the fact that the silver-content has been modified from time to time. Anglo-Saxon and Anglo-Norman silver coins are believed to have contained 92·5 per cent. of silver. This standard remained the same until the 34th year of the reign of Henry VIII, when a great fall took place. A still deeper fall in the standard fineness ensued in 1545, and again in 1546 and in the reign of Edward VI. In the fourth year of that King's reign it reached its lowest point, namely, 25 per cent. of silver. Strangely enough, this base coinage was projected with a view to secure by the transaction the sum of £160,000 to be devoted to the restoration of the standard generally. Half this sum appears to have been actually obtained. In 1552 the standard was restored to nearly its original richness, or 92·1 per cent. of silver. This standard was maintained during the reigns of Queen Mary and Queen Elizabeth. The coins circulated in Ireland during the latter reign were deplorably poor in silver, and consisted of 24·1 per cent. of silver and 75·9 per cent. of copper. The standard for silver coins was raised to 92·5 per cent. in the reign of Queen Elizabeth and was not debased again until 1920.

In 1920 an Act permitted the silver in coins to be reduced to 50 per cent., the remainder being an alloy consisting largely of nickel, but containing some copper. These coins tended to become yellow and discoloured when they were worn. In 1925 the 50 per cent. of alloy was maintained, but the copper-content was reduced to a mere trace. This is the standard silver at present in use, namely, 50 per cent. of silver and 50 per cent. of an alloy consisting of nickel and a trace of copper.

RECORDED CASES OF COUNTERFEITING.—As has already been indicated, most of the published references to cases of coining come from outside Britain. A number of counterfeit silver coins were circulated in Palestine in 1924. They had been cast and had a low density; they contained a deficiency of silver and an excess of copper. Some of the coins, however, were of normal density and silver-content but were undoubtedly counterfeit.[2]

In a note by Matthews[3] a description is given of a counterfeit half-crown piece. It was a moulded coin consisting of 97·33 per cent. of tin and 2·67 per cent. of copper and was much lighter than a genuine half-crown.

After the introduction, in 1927, of the new Palestine currency, counterfeit coins were much in evidence. In 1928, 34 coins were found to be counterfeit. They contained considerably more silver than the genuine currency, had been cast, and were slightly smaller than genuine coins.[4]

In 1929, 77 coins were found to be counterfeit. Most of these were similar to those found in the previous year. Two, however, were found to be exceptionally well made. They had been struck—not cast—and contained approximately 57 per cent. of silver. On one occasion in Haifa a large number of 100-mil pieces of pure tin were discovered by the police, together with iron moulds and sticks of pure tin.[5]

In Ceylon, seven cases of counterfeiting were investigated. The moulds used consisted of two flat pieces of cuttle-fish bone, between which the genuine coin was impressed. No details of the composition of the coins were given.[6]

The most obvious fault in the counterfeit coins found in Palestine in 1930 was generally in the milling. Either file marks or a blank could be detected at one place on the circumference, presumably where the "tail" had been removed.[7]

During 1930, in the Federated Malay States, 1533 counterfeit coins were found. The moulds used had been made of plaster of Paris.[8]

In Cyprus, 54 counterfeit coins were examined in 1930. They either consisted of pure tin or contained excessive quantities of silver, varying from 60 to 80 per cent. This high percentage was probably due to the low price of silver at that time.[9] In Cyprus, in 1932, three types of coins were found. Eight consisted of silver and copper, 11 of lead and tin, and 6 of tin. Two counterfeit English "silver" coins of excellent design were found to consist of pure tin.[10]

In the Straits Settlements in 1933 complete outfits for making coins were found. The usual alloys consisted of lead, tin and antimony, but one lot of coins was made of an alloy of zinc, copper and aluminium, and another lot was made from chandu tubes. A silver-copper alloy had been used for 26 Straits Settlements 10-cent pieces, and 5 Dutch East Indian half-guilders.[11]

In Palestine, in 1933, a large number of spurious coins (758) were tendered on the railways. Some were cast and some were struck. These were cleaned with dilute ammonia and examined by low-power microscopical methods. In this way 9 different dies were identified. It was found that 67 per cent. of the struck coins were made by the same people. The size, diameter, weight and appearance were approximately correct and would have readily deceived all but experts.[12]

In Palestine, in 1934, a counterfeiter was convicted on the evidence that the moulds and coins found on his premises corresponded with some counterfeit coins found. Enlarged photographs proved the correspondence of the coins found in his house with the dies used.[13]

In Hong Kong, in 1935, coins found consisted of 5 parts of tin, 2 of antimony and 1 of copper.[14] A large number of counterfeit coins were also found in 1936. They were purported to be the new 1935 mixed metal 10-cent pieces. Most of them were made of an alloy of the German silver type. These were struck, not moulded, and had minor faults. In one case, the actual die and presses for making the coins were discovered. They were counterfeit Queen Victoria 5-cent pieces and were of silver-plated copper. They were very good copies and the die had been very carefully made.[15]

SCOTTISH CASES.—A few years ago some very skilfully made counterfeit half-crowns were circulated in Edinburgh. They actually contained more silver than genuine coins of the same date (1920) and had a "ring" very similar to that of genuine coins. Their design was so nearly perfect that they had been passed as genuine by several banks and post offices. The counterfeiters endeavoured to get rid of several of the coins by purchasing postal orders, and suspicion was aroused by the number of these asked for at a small post office in Leith Street. A casual observer would never have noticed anything wrong with the coins, as the only imperfection was in the milling, where two of the ridges came too close together. This was only discovered when some of the coins had been returned to the mint. Coining cases in Edinburgh are fortunately of somewhat rare occurrence. About 30 years ago a coiner was convicted for making and circulating some 4s. pieces. These, on analysis, were found to consist almost entirely of tin.

In December, 1938, the Edinburgh police apprehended a man on the charge of making and circulating counterfeit coins. On raiding his house, they seized a number of coins and articles which were alleged to have been used for making counterfeit coins. The articles examined constituted a rather extraordinary and miscellaneous collection. There were 7 half-crown pieces, a suit case, 9 moulds of plaster of Paris, 10 pieces of plaster of Paris, a packet of "blanco," an aluminium pan, 5 tin cans containing metal, a dessert spoon, a piece of scrap white metal, a white enamel basin, pieces of matting, two empty coal bags, and a stout metal knitting needle.

The seven half-crown pieces were very similar in appearance, being fairly crudely made and having a bluish colour. They were undoubtedly counterfeit and would not readily have deceived anyone who looked at them critically. On analysis, they were found to contain no silver, nickel or copper, but to consist of an alloy of lead and tin. The weights of the coins were 202·65 grains, 208·96 grains, 205·56 grains, 210·25 grains, 209·40 grains, 206·70 grains, and 218·95 grains. As the standard weight of a new half-crown is 218·181 grains, it will be observed that all the coins, except the last, are distinctly under weight, and that the last one is too heavy to be genuine. As a rule, moderately worn half-crown pieces are rarely more than 5 grains short in weight.

The coins were dated 1929 and 1933, and showed evidence of having been cast. They did not ring when dropped on a hard surface, and showed imperfections on their surfaces and on the milled edge where the runner had been removed. The specific gravity of six of the coins was about 9·0, and they contained about 60 per cent. of lead and 40 per cent. of tin. The other coin was found to contain a larger percentage of lead and had sp.gr. 9·65, which was very similar to that of a genuine silver coin. All the coins made a mark when rubbed on paper, thus indicating their large content of lead; traces of iron and zinc were also present. A similar alloy consisting of lead and tin was also found in the various articles. Old condensed milk tins had been used for melting the alloy, and these were fashioned so as to have narrow beaks to facilitate pouring into a small aperture. The moulds, found to be made of plaster of Paris, had been shaped by making in match-boxes. These moulds were in two halves, which fitted into each other with a number of joints. They had depressions in the centre between the halves, which indicated that they had been used for moulding coins. Six of the moulds were small and appeared to have been used for moulding shillings. The other two were larger and showed evidence of having been used for moulding florins. All these moulds were of a type that could be used for casting counterfeit coins.

They were not nearly perfect and may have been discarded because of faults. Coin markings were noted on some, but in the condition in which they were found they would have been useless for moulding purposes. One of the exhibits was one-half of a complete mould. It was about the size of a small match-box and showed a very good impression of a shilling piece. Some pieces of broken moulds of a larger size showed impressions indicating that they had been used for casting half-crown pieces. There was no evidence, such as might be afforded by the presence of lead or tin, to indicate whether these moulds had actually been used. Among the articles found in the house of the accused was a piece of metal, which, on analysis, was found to consist of an alloy of lead and tin of exactly the same specific gravity and composition as the heaviest counterfeit half-crown piece found.

The conclusions arrived at from the examination of all the coins and exhibits connected with this case were as follows:

The coins were all counterfeit, were rather crudely made, and had been cast out of a metal alloy resembling solder. They contained no silver, nickel or copper, and would not readily be mistaken for genuine coins, except in the dark. The moulds consisted of plaster of Paris and were of a type which can be used successfully for casting coins. The small aluminium pan and tins contained metal and showed distinct evidence of having been used for melting the lead-tin alloy, and the manner in which the spouts were made narrow and pointed indicated that their use was for pouring the metal into a small opening such as existed in the moulds. The rug and sacks taken from the house of the accused also showed evidence of their association with the use of melted lead-tin alloy.

The accused was charged under the Coinage Offences Act, 1936. For an offence of this kind a person could receive a sentence of as much as five years' imprisonment. He pleaded guilty to three charges of tendering counterfeit coins, and was sentenced to 15 months' imprisonment.

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Examination of Fatty Material taken from an Egyptian Tomb at Armant

By T. P. HILDITCH, D.Sc., F.I.C.

In the spring of 1937 Dr. O. H. Myers, of the Egypt Exploration Society (Sir Robert Mond Expedition), submitted for examination material taken out of a pot dating from about the fifteenth century B.C. from a grave at Armant. Dr. Myers stated that it came from an entirely undisturbed burial, that there was no doubt as to its date or authenticity, and that it was by far the best preserved example of ancient grease he had encountered.

The specimen consisted of a block, about 500 g. in weight, and shaped somewhat like a loaf. It consisted of hard material, firm and homogeneous in texture, but with a distinctly greasy feel when rubbed between the fingers. It was brownish-cream in colour, except for the exterior which, to a depth of 2–3 mm., was dark brown. It was almost odourless, apart from a very faint smell reminiscent of rancid coconut fat.

Most of the specimen (450 g.) was broken into pieces of about the size of a small pea and extracted exhaustively in a Soxhlet apparatus with light petroleum (b.p. 40–60° C.), which removed 270 g. of a cream-coloured hard fat that melted at about 50° C. and had acid value 84·1, saponification equivalent 273·6 and iodine value 1·5. The material contained, therefore, about 60 per cent. of compounds of a fatty nature which, although including about 40 per cent. of free fatty acids, were quite pale in colour and possessed only a very faintly rancid odour. The portion insoluble in light petroleum was a brown solid, no longer greasy to the touch, but somewhat elastic (in this respect resembling fragments of cork).

Examination of the Portion Soluble in Light Petroleum.—The acids resulting from the hydrolysis of 101·6 g. of this portion were distilled in steam (which removed only 0·1 g. of acids recoverable by extraction with ether) and yielded 98·1 g. of fatty acids non-volatile in steam. These were converted into methyl esters and fractionally distilled at 0·2 mm. from a Willstätter flask, with the results shown in Table I.

The component acids of the material soluble in light petroleum, from the data in Table I, are made up of myristic (?) 0·7, palmitic 36·5, stearic 59·1, arachidic (?) 1·3, and oleic 2·4 per cent. (weight).

Examination of the Portion Insoluble in Light Petroleum.—The appearance and texture of this part of the material was reminiscent of that of a highly "blown" or air-oxidised oil and led to the suspicion that in part, if not entirely, it might have been originally part of the fat present in the original material. If so, it would represent the debris produced by slow atmospheric oxidation of mixed saturated–unsaturated glycerides originally present; the original unsaturated acyl radicals, now converted into oxidised and perhaps polymerised acyl groups, might still be linked as mixed glycerides with saturated acyl groups present in the original molecules of the fat. On saponification, a product of this nature would yield a further quantity of saturated acids (soluble in light petroleum) as well as oxidised products of the unsaturated acids (probably insoluble in light petroleum).

TABLE I

No.	g.	B.p./0·2 mm.	Saponification equiv.	Iodine value
		Primary fractionation		
1	31·1	75–139°	270·6	1·3
2	9·0	139	283·4	1·5
3	9·4	139	287·3	1·6
4	7·8	139–142	291·3	1·8
5	8·2	142	293·9	2·0
6	8·7	142–145	295·5	2·0
7	7·8	145–149	295·5	2·0
8	4·5	149	299·3	3·2
9	5·0	Residue	302·4	6·8
	91·5			
		Refractionation of fraction No. 1		
11	3·3	100–129°	227·5	1·0
12	3·8	129–130	267·3	0·8
13	4·9	130	271·0	0·8
14	5·5	130	275·2	1·0
15	5·2	130	283·0	1·5
16	4·6	Residue	292·9	3·8
	27·3			

A portion (130 g.) of the fraction of the original specimen insoluble in light petroleum was therefore hydrolysed with boiling alcoholic potash, and the resulting acids (57 g.) were liberated and treated with light petroleum (b.p. 40–60° C.), when the following separation was effected:

Acids	Soluble in light petroleum "A"	Insoluble in light petroleum "B"
Weight, g.	18·5	38·5
Mean equivalent ..	227·3	196·7
Iodine value ..	4·4	6·3

The acids "A" were typical crystalline fatty acids, whilst "B" were dark in colour and resinous in appearance. Each group was converted into methyl esters and distilled at 0·2 mm. through an electrically-heated, packed glass column, with the results shown in Table II.

The onset of distillation in both groups of esters was accompanied by evolution of gas; this is characteristic of air-oxidised oils and their derivatives.[1]

The acids from fraction A1 yielded, on crystallisation, small quantities of azelaic and palmitic acids and also a fraction which appeared to contain myristic acid.

The acids from the residual fraction A6, after oxidation with dilute alkaline potassium permanganate, gave a small amount of 9,10-dihydroxystearic acid, m.p. 127–128° C., indicating the presence of oleic acid in this fraction.

The esters from group B, when dissolved in ether, gave solutions which were miscible with water, and had to be washed with sodium chloride solution. The large residual, undistilled fraction of these esters was a spongy mass, typical of the esters of air-oxidised ("blown") oleic acid. Fractions B2 and B3 were oxidised with dilute alkaline permanganate, but failed to yield any 9,10-dihydroxystearic acid. All these characteristics, and the boiling-points, saponification equivalents and iodine values of fractions B3, B4 and B5, are closely similar to those observed in the distillation of methyl oleate which has been oxidised by agitation with a current of air.[2]

TABLE II

No.	g.	B.p.	pressure	Saponification equiv.	Iodine value
		Methyl esters of acids "A"			
		°C.			
A1	2·1	70–106	0·2 mm.	140·7	4·8
A2	2·1	106–116	,,	250·5	3·0
A3	2·7	116		263·4	3·6
A4	2·9	116–130		287·6	4·3
A5	2·8	130–150		288·5	7·8
A6	3·5	Residue		289·3	18·0
	16·1				
		Methyl esters of acids "B"			
B1	2·4	120	15 mm.	115·5	4·3
B2	1·8	120 (falling)	,,	176·7	28·3
B3	2·1	140–160	0·2 mm.	250·9	25·7
B4	2·2	160 (falling)	,,	254·3	34·6
B5	1·5	*	,,	255·1	28·1
B6	15·5	Residue	,,	Not determined	
	25·5				

* Esters held up on packing of column.

On the other hand, the acids of group A, apart from the presence of a little oleic acid and of a certain amount of acids of low molecular weight (obviously scission-products of oleic acid, and taken for the purpose of approximate calculation as azelaic acid), are simply the usual mixture of saturated acids—palmitic and stearic with probably small proportions of myristic. The total acids in fraction A were computed to be (approximately) azelaic 8, myristic 8, palmitic 42, stearic 33, and oleic 9 per cent. (weight); so that the proportions of the higher saturated acids found were, approximately, myristic 10, palmitic 50, and stearic 40 per cent. (weight).

GENERAL CONCLUSIONS.—The specimen has been shown to contain about 35 per cent. of neutral fatty matter of mainly saturated character, about 25 per cent. of free, mainly saturated, fatty acids, and about 40 per cent. of material insoluble in light petroleum. The last, however, after treatment with alcoholic potash, yielded about half its weight of acidic material, about one-third of the latter being saturated acids soluble in light petroleum and evidently present in the original insoluble matter in combination (as mixed glycerides) with the air-oxidised unsaturated groups of the mixed saturated–unsaturated glycerides of the original fat.

It is considered that this evidence establishes that the specimen originally consisted, to the extent of at least 80 per cent., of fat. It is further likely that the remainder of the material consisted of triolein, which had broken down completely by the prolonged action of the atmosphere into nonanoic and azelaic acids, or even simpler degradation products of a water-soluble character.

The chemical composition of the fatty matter which had survived resembled that of other specimens of fats from Egyptian tombs examined previously (Chaston Chapman and Plenderleith,[3] Banks and Hilditch[4]). It was almost wholly saturated in character. The component acids present (37 per cent. of palmitic and 59 per cent. of stearic acid in the portion soluble in light petroleum, and 10 per cent. of myristic, 50 per cent. of palmitic and 40 per cent. of stearic acid in the products of hydrolysis of the residual insoluble portion) point, as in the previous specimens, to an animal depot fat, probably of the ox, sheep or goat. Dr. Myers states that the material fitted tightly into its containing bowl as though it had been poured in in the liquid condition, and it seems extremely probable that the specimen was originally an ox, sheep or goat fat which had been melted and poured into the bowl. It may be significant that at the present day melted fats from these sources are still used extensively in native Egyptian cooking.

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A New Method for the Gravimetric Determination of Tin in Bronzes and Brasses

BY A. G. DUNBAR-POOLE

THE usual method for the gravimetric determination of tin in bronze and brass consists in treating the alloy with nitric acid and igniting the insoluble residue. Owing to the adsorptive properties of the hydrated stannic oxide the precipitate will contain most of the phosphorus and arsenic present in the alloy. Small impurities of iron and antimony, if present, will also be entrained by the precipitate. Therefore, when an accurate figure for the tin-content of an alloy is required, account has to be taken of the associated impurities of the stannic oxide.

With a brass in which the tin and iron are present in approximately similar proportions, say, 1 to 2 per cent., it has been found that hydrolysis is effected only after boiling the stannic solution for a long time and allowing it to stand. Iron will be present in the precipitate, and some of the tin may be in solution. When a complete analysis of the alloy is being carried out, a deduction in weight may be made for the impurities assumed to be present in the oxide. This, however, is unsatisfactory because, in a phosphor-bronze, some of the phosphorus will invariably be found in the filtrate, and when the precipitate is ignited a loss of arsenic may occur; hence the assumption that the whole of the phosphorus and arsenic is associated with the precipitate is incorrect.

Another method in use is to fuse the impure stannic oxide with a mixture of sodium carbonate and flowers of sulphur, to extract it with water and to remove the sulphides of copper, lead, and iron. One drawback to this method is that several fusions are needed to dissolve all the stannic oxide if this is present in quantity.

The principle involved in the following method is based upon the discovery that when tin containing phosphorus or arsenic, or both, is ignited in air in presence of copper, the phosphorus and arsenic are taken up by the copper to form a phosphate and arsenate respectively, without the formation of a stannate. A subsequent digestion in nitric acid leaves the insoluble tin oxide, whilst the copper, phosphorus, and arsenic go into solution.

In tests on phosphor-bronze, containing, say, 12 per cent. of tin and 1 per cent. of phosphorus, it has been found that by digesting the sample in the minimum quantity of nitric acid, evaporating the solution to dryness, igniting the residue at a red heat, and again digesting it in nitric acid, a residue of pure tin oxide is obtained.

Furthermore, if the sample of phosphor-bronze is obtained in a state of fine division, it may be ignited direct (with a little lime to prevent it from sticking to the crucible) at a bright red heat, cooled and digested in nitric acid and the insoluble tin oxide recovered; this will represent the whole of the tin-content of the sample and be free from phosphorus and arsenic.

When this procedure was applied to a copper-tin alloy in which iron was present to the extent of, say, 1 per cent., it was found difficult to free the oxide of tin from associated iron, and complete separation could be effected only by a long and tedious extraction with acid.

Experiments were then made in which the alloy was dissolved in *aqua regia*, excess of ammonia solution was added, and the solution was acidified with sulphuric acid and boiled with sodium thiosulphate, which reduced and prevented precipitation of the iron, and converted the copper into copper sulphide.

The precipitate, which included all the tin, phosphorus, arsenic and antimony intimately mixed with the copper sulphide, was filtered off, washed and ignited in air. It was then digested in nitric acid, whereby the copper together with the soluble phosphate and arsenate was readily dissolved, whilst the insoluble, pure, tin oxide (and antimony, if present in the alloy) was left.

METHOD.—The details of the method finally adopted are as follows:—For bronze in which the tin-content is considerable 0·5 g. of the drillings is dissolved, at a gentle heat, in 15 ml. of nitric acid (sp.gr. 1·20) and 5 ml. of dilute (1:1) hydrochloric acid in a 400-ml. tall beaker. The beaker is rinsed, the solution is diluted slightly with water, and ammonia solution (1:1) is added in excess, *i.e.* until a deep blue solution results. This solution is neutralised with sulphuric acid (1:3) and 2 ml. in excess are added, after which it is diluted with hot water to about 300 ml. and boiled, and while boiling treated with 4 g. of sodium thiosulphate dissolved in about 50 ml. of water. Boiling is continued gently for 15 minutes (with longer boiling the iron may be re-oxidised and precipitated), the precipitate is allowed to settle, the hot solution is filtered through a 12-cm. Swedish 1F (or Whatman 540) paper, and the precipitate is washed three or four times with hot water containing a little ammonium sulphate.

The precipitate is ignited, the ignition being carried out at first slowly at the mouth of a muffle, and finally at a red heat until all the copper is converted into oxide. The precipitate is then brushed out into a squat 150-ml. beaker, covered with about 25 ml. of conc. nitric acid, and digested until the copper has completely dissolved. The solution is diluted with water to approximately 100 ml., and the precipitate is allowed to settle while the liquid is kept hot. It is then collected on a Whatman No. 44 filter-paper, washed with a little hot dilute nitric acid and finally with hot water, ignited and weighed.

Any trace of antimony that was present in the alloy will still be present. Its presence will be indicated by the blue colour that it imparts to the ignited tin oxide. If the precipitate is white, or nearly so, the absence of antimony is assured. As the amount of antimony in the precipitate increases, the blue colour becomes more intense, until, with a considerable percentage present, the ignited precipitate will be almost black.

Should the amount of antimony present make a separation from the tin desirable or necessary, the ignited precipitate may be fused with sodium hydroxide in a silver crucible, the melt extracted with water, alcohol added, and the precipitated sodium antimonate collected (method of H. Rose), or, the aqueous extract may be acidified with hydrochloric acid and boiled with a sulphite to reduce the antimony, which is determined volumetrically by re-oxidation.

In applying the method to a brass containing only a low percentage of tin it is desirable to use a greater weight of the sample. At the same time it is inconvenient to precipitate the whole of the copper as sulphide from, say, 2 g. of the alloy. Therefore 2 g. of the sample may be dissolved in nitric and hydrochloric acids as described above, the tin, iron, etc., precipitated as hydroxides by the addition of ammonia solution, and the solution heated to boiling and filtered through a paper filter (Whatman 541 or similar paper). The precipitate is washed back into the original beaker, 2 or 3 ml. of hydrochloric acid are added, and the solution is heated until clear. Ammonia solution (1:1) is added in excess, the solution is neutralised with sulphuric acid (1:3), 2 ml. in excess being added, and 2 g. of copper sulphate dissolved in a little water are introduced. Four g. of sodium thiosulphate dissolved in about 50 ml. of water are added, and the process is continued as described in the method for bronze.

Results.—The following results were obtained with samples prepared by dissolving mixtures of the pure metals, etc., shown below. No. 1 represents a typical phosphor-bronze, No. 2 a gun metal, and Nos. 3 and 4 brasses.

	Amount taken		SnO$_2$ found	
	g.	Per Cent.	g.	Tin Per Cent.
1.				
Pure tin	0·0605	12·10	0·0770	12·12
» iron	0·005	1·0		
Phosphorus (as ammonium phosphate)	—	1·0		
Arsenic (as arsenic chloride) ..	—	1·0		
Pure copper	0·425	85·0		
2.				
Pure tin	0·053	10·60	0·0700	11·02 (tin + antimony)
» iron	0·010	2·00		
» lead	0·01	2·00		
» antimony	0·002	0·40		
Manganese	—	1·00		
Phosphorus	—	1·00		
Arsenic	—	0·50		
Pure copper	0·4025	80·5		
» zinc	0·01	2·0		
3.				
Pure tin	0·0208	1·04	0·0268	1·06
» iron	0·02	1·00		
» lead	0·02	1·00		
Manganese (as manganese sulphate)	—	1·00		
Arsenic (as arsenic chloride) ..	—	1·00		
Pure copper	1·3	65·0		
» zinc	0·6	30·0		
4.				
Pure tin	0·0400	2·00	0·0565	2·22 (tin + antimony)
» iron	0·02	1·0		
» lead	0·02	1·0		
» antimony	0·0044	0·22		
Phosphorus	—	1·0		
Arsenic	—	0·5		
Pure copper	1·48	74·0		
» zinc	0·4	20·0		

Results No. 3 and 4 were obtained by removing the tin from the bulk of the copper by precipitation with ammonia solution (as described).

I desire to acknowledge my indebtedness to the Director of Scientific Research for granting permission to publish this method.

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Quinaldinic Acid as a Reagent for the Separation and Determination of Copper and Cadmium

By ANIL KUMAR MAJUMDAR

QUINALDINIC acid was introduced by Rây and Bose[1] as a reagent for the determination of copper, zinc and cadmium. It was shown that copper could be separated from cadmium, lead, manganese, nickel, cobalt and acids of phosphorus and arsenic by this reagent in presence of a suitable quantity of mineral acids.

Recently, however, Shennan[2] has called in question the suitability of the reagent for the separation of copper from cadmium, but followed a method entirely different from that recommended by Rây and Bose. Shennan employed a buffer of sodium acetate and acetic acid and, operating over a *p*H range of 2·69 to 3·11, obtained high results. This is obvious from a perusal of Rây and Bose's work, in which a much lower *p*H range was maintained for the purpose of separation by the use of mineral acids. The present investigation was undertaken with the object of testing the validity of Rây and Bose's method and of determining the *p*H range over which the separation of copper from cadmium, if practicable, can be effected.

Shennan has shown that copper can be completely precipitated over the *p*H range 2·5 to 6·96, and that the range could be extended to *p*H 1·5; though, curiously enough, he did not make any attempt to separate copper from cadmium at *p*H values lower than 2·69.

It was considered desirable, therefore, to determine the *p*H range over which Rây and Bose made their separation, that is, the range corresponding with 2 to 10 ml. of 2 *N* sulphuric in a total volume of 170 to 180 ml. The *p*H of the filtrate from the precipitation of copper was measured in each test by means of the quinhydrone electrode.

PROCEDURE FOR THE DETERMINATION OF COPPER.—Electrolytic copper (2·1183 g.) was dissolved in nitric acid, which was then removed by evaporation with sulphuric acid. The solution was made up to 500 ml. in a standard measuring flask. The copper-content of the solution was electrolytically determined. Five or 10 ml. of the copper solution were neutralised with dilute ammonia, and copper was precipitated with sodium quinaldinate (1 g. of quinaldinic acid per 100 ml. of solution) in presence of 2 to 10 ml. of 2 *N* sulphuric acid in a total volume of 170 to 180 ml. exactly according to the method prescribed by Rây and Bose (*loc. cit.*). The results are given in Table I.

The minimum *p*H attained in the above series, with complete precipitation of copper, is 1·22, and the maximum reached is 2·01. Rây and Bose's method for the separation of copper from cadmium was evidently confined within this range, which is considerably lower than that of Shennan's experiment.

SEPARATION OF COPPER FROM CADMIUM.—Table II shows a few results of the separation of copper from cadmium by Rây and Bose's method over the *p*H range

2·15 to 2·01, the maximum in Table I. Only 2 ml. of 2 *N* sulphuric acid were used in this series of experiments. A solution of Kahlbaum's cadmium sulphate of analytical reagent quality was prepared and its cadmium-content (as sulphate) was determined. The strength of the reagent solution was identical with that employed for the individual determinations of copper as described above. In the filtrate cadmium was determined as quinaldinate by Rây and Bose's method (*loc. cit.*).[2]

TABLE I

2 *N* Sulphuric acid ml.	Reagent ml.	Wt. of ppt. g.	Copper present g.	Copper found g.	*p*H
2	20	0·1416	0·02118	0·02118	2·01
4	20	0·1414	0·02118	0·02115	1·46
4	18	0·1416	0·02118	0·02118	1·45
6	25	0·1416	0·02118	0·02118	1·40
6	20	0·1416	0·02118	0·02118	1·35
8	30	0·1416	0·02118	0·02118	1·31
8	25	0·1413	0·02118	0·02114	1·27
10	35	0·1418	0·02118	0·02121	1·25
10	35	0·1416	0·02118	0·02118	1·25
10	30	0·1416	0·02118	0·02118	1·22

TABLE II

*p*H	2 *N* ml.	Reagent ml.	Wt. of copper ppt. g.	Copper present g.	Copper found g.	Cadmium present g.	Cadmium found g.
2·01	2	20	0·1416	0·02118	0·02118	0·05111	0·05096
2·01	2	20	0·1418	0·02118	0·02121	0·05111	0·05098
2·15	2	40	0·2826	0·04236	0·04228	0·10220	—
2·15	2	40	0·2831	0·04236	0·04235	0·10220	0·10214

From these results it is obvious that the separation is complete and no confirmation for results at lower *p*H values down to 1·22 (10 ml. of 2 *N* H_2SO_4) is required. Shennan's statement, that quinaldinic acid is unsuitable for the separation of copper from cadmium, is thus shown to be incorrect.

That copper cannot be separated from zinc, or zinc from cadmium, by this reagent was already stated by Rây and Bose in their first paper, and Shennan's work only confirmed that statement. As a matter of fact, a method for the separation of zinc from copper by quinaldinic acid has recently been published by Rây and Dutt, and by Rây and Sarkar.[4]

In this connection it might be pointed out that the alternative method suggested by Rây and Bose for the separation of copper from cadmium by free quinaldinic acid in presence of acetic acid has always been found to give high results, owing to co-precipitation of cadmium. But, as the results obtained by Rây and Bose by this method are as good as those given by the sulphuric acid method, it is quite probable that their test solution might have contained some mineral acids, which kept the *p*H value within the proper range. With free quinaldinic acid in presence of 2 ml. of acetic acid, other conditions remaining unchanged, the *p*H of the filtrate from the copper precipitate in the separation of copper from cadmium was found to be as high as 2·57.

It is interesting to note here that copper quinaldinate is appreciably soluble in acetic acid. A few determinations of copper in presence of 35 ml. of glacial acetic acid (*p*H = 2·2) without any sodium acetate gave results 0·6 per cent. too low, and the filtrate gave a fairly large precipitate with rubeanic acid after neutralisation with ammonia. Even with 10 ml. of acetic acid the filtrate was not free from copper. This solubility, however, is considerably reduced by the addition of sodium acetate. That the effect is specific and has nothing to do with the *p*H value is proved by the fact that copper is completely precipitated in presence of mineral acids, even at *p*H 1·22.

Shennan's statement, that sodium acetate has a pronounced solubilising effect, is not correct—rather the contrary. This is also evident from his own results.

My thanks are due to Professor P. Rây for his interest in this work and for the facilities I have received for conducting it in his laboratory.

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INORGANIC CHEMISTRY LABORATORY
UNIVERSITY COLLEGE OF SCIENCE
CALCUTTA

August, 1939

Notes

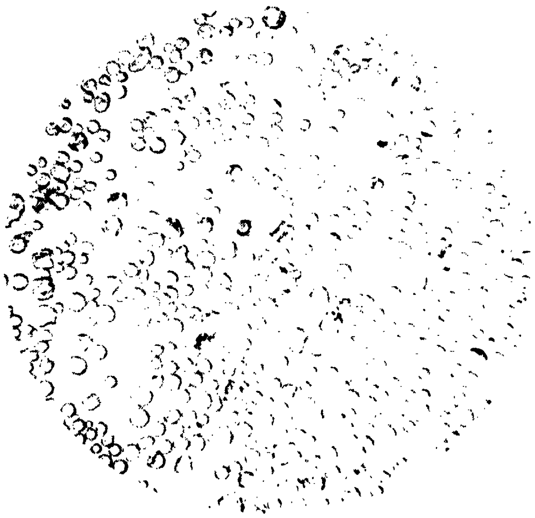
The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A SEMI-MICRO-ANALYTICAL METHOD FOR THE DETERMINATION OF METHOXYL GROUPS IN ORGANIC COMPOUNDS

THE determination of methoxyl groups in organic compounds by the normal Zeisel method is a lengthy procedure. A rapid semi-micro method, based on the Zeisel method, was consequently adopted and gave satisfactory results. The methoxyl group was removed as volatile methyl iodide by the action of hydriodic acid at 130° C. The vapour was passed over a test-paper which had been previously steeped in a solution of palladium chloride and pyridine. A brown colour on the paper indicated the presence of a methoxyl group.

The apparatus used consists of a 50-ml. flat-bottomed flask fitted with a side tube and having a ground-glass neck. A glass tube, 18 cm. long and of 0·7 cm. bore, fits into the neck of the flask, and the top of this tube ends in a disc-like flange, 2 cm. in diameter and 0·4 cm. thick, the top of which has a ground surface. A similar glass flange rests on this surface, and is attached to a glass tube, 3 cm. long. The two flanges are held in position by means of two steel clips.

PROCEDURE.—A known weight of the organic compound (about 0·5 g.) is dissolved in decahydro-naphthalene of analytical reagent quality, and the volume is made up to 50 ml. A convenient aliquot part of this solution (*e.g.* 0·5 ml.) is then placed in the flask of the apparatus together with 5 ml. of pure hydriodic acid (sp.gr. 1·7). The glass tube is placed in position, a strip of No. 4 Whatman filter-paper saturated with the palladium chloride and pyridine solution is placed



Starch from Unripe Tomatoes
× 150

between the two glass flanges and the clips are adjusted. A slow stream of pure carbon dioxide is passed through the side tube of the apparatus. The gas must have been dried by passage through pure glycerin, and heated to 35° C. by passage through a wash-bottle immersed in a bath of hot water. The flask is heated in an oil-bath at 130° C. and shaken frequently. After 30 minutes it is disconnected, and the test-paper is removed and allowed to dry, after which it is compared with previously prepared standards and the percentage of methoxyl group is calculated.

PREPARATION OF STANDARD PAPERS.—Vanillin (0·4903 g.) is dissolved in 100 ml. of decahydro-naphthalene; 0·1 ml. of this solution (containing 0·0001 g. of methoxyl group) is treated as described above. A series of standard papers representing increments of 0·1 ml. is prepared.

PALLADIUM CHLORIDE AND PYRIDINE SOLUTION.—One g. of palladium chloride is dissolved in 60 ml. of water and 10 ml. of hydrochloric acid. Thirty ml. of pyridine are added and the solution is filtered. The test-papers are steeped in the solution immediately before use and used while damp.

RESULTS.—The following results illustrate the accuracy of the method:

	Methoxyl group	
Compound	Theoretical Per Cent.	Determined Per Cent.
Anisole	28·70	28·0
Eugenol	18·90	18·5
Guaiacol	25·00	24·3

E. B. LISLE

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STARCH FROM UNRIPE TOMATOES

SINCE the publication of my note on the starch of immature linseed (ANALYST, 1939, 735) Mr. James Smith, of Liverpool, has called my attention to another little-known starch—that from unripe tomatoes. The microscopical appearance of this starch closely resembles that of the starch from sweet potato and from immature linseed.

He has kindly allowed me to use the accompanying photomicrograph, the magnification of which is × 150.

F. ROBERTSON DODD

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NESSLER CYLINDERS OF LEAD GLASS

ARISING out of Mr. T. McLachlan's note in THE ANALYST of September, 1939, the following extract from the "British Standard Specification for Nessler cylinders, No. 612—1935" may be of interest:—"The cylinders shall be made of glass, shall be as free as possible from striae and similar defects and shall be well annealed. If lead glass is used for the cylinders the words 'Lead Glass' shall be inscribed on them."

The difficulty referred to by Mr. McLachlan should therefore not arise with British Standard Nessler cylinders.

BRITISH STANDARDS INSTITUTION
28, VICTORIA STREET
LONDON, S.W.1

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Report of the City Analyst for the Second Quarter, 1939

Of the 1386 samples submitted under the Food and Drugs Act, 19 were bought formally.

Sodamint Tablets.—Two samples of these tablets were not made in accordance with the B.P. Codex formula, which requires them to contain ammonium bicarbonate and saccharin in addition to sodium bicarbonate and peppermint oil. These are further instances of the unfortunate confusion arising from the fact that the name "soda mint" has been applied to tablets made up to different formulae. It is surely not impossible to arrange that a specific name should always connote the same mixture of ingredients and to ensure that a customer will always be supplied with the same article wherever he makes his purchase.

H. H. Bagnall

CITY OF LEICESTER

Report of the City Analyst for the Year 1938

Oxidation and Iodine Values of Vinegars.—A number of samples were tested by the method of Edwards and Nanji (Analyst, 1939, **63**, 410), with the following results:

Sample	Oxidation value	Iodine value	Nitrogen Per Cent.	Phosphate
Malt vinegar	755	1052	0·053	+
,,	664	728	0·072	+
Vinegar	842	404	0·069	+
,,	4·5	4·8	0·009	—
,,	1302	904	0·056	+
,,	400	492	0·103	+
,,	592	832	0·074	+
,,	381	836	0·070	+
,,	3·2	5·8	—	—

The two samples with low oxidation and iodine values were reported against as consisting of artificial vinegar.

Metallic Contamination.—*Tin in Sugar.*—After correspondence with the Ministry of Health, the wholesalers and the West India Committee, it was decided for the time being to adopt a maximum standard of two grains per lb. without prejudice to revision at some future date. Three samples of Demerara sugar contained respectively, 0·66, 1·1 and 1·25 grains of tin, and one sample of brown sugar contained 3·1 grains per lb.

Zinc in Ice-cream.—Four samples from one manufacturer contained small quantities of zinc, the highest being 0·66 grain per lb. It transpired that the mix before freezing had been allowed to ripen for 24 hours in ordinary zinc galvanised buckets.

Copper in Yeast Extract.—Two samples of one preparation contained 37 and 20 parts of copper per million and two samples of another preparation each contained 60 p.p.m. One of the manufacturers blamed the brewer who supplied the yeast, and took the attitude that, as yeast was a by-product of the brewery, he could not be expected to take any trouble to ensure the absence of copper or anything else. He undertook, however, to replace copper plant with stainless steel and monel metal.

Copper in Coffee and Chicory Essences.—Nineteen samples of coffee and chicory essence contained from 8 to 37 parts of copper per million. Present information seems to show that the copper is presumably all derived from metallic apparatus used in manufacture.

Dandelion Coffee.—A sample of dandelion coffee contained 15 parts of copper per million, and 6 samples of dandelion coffee essence contained from 4 to 50 p.p.m. (average 16 p.p.m.). The sample containing 50 p.p.m. was sold as a "Health Food," with a label specially recommending it "for those suffering from weak stomachs, dyspepsia and indigestion." As a result of representations to the manufacturer, he undertook to use earthenware vessels in extracting the root.

BACTERIAL PURITY OF WATERCRESS.—A sample, submitted privately with a complaint of bad smell and presence of duckweed, was found to be highly contaminated with coli-aerogenes organisms. For convenience, the counts were reported as so many per sprig (one sprig representing 3 g. of cress). A check sample from the same source gave a very similar result, the coli-aerogenes organisms amounting to about 100 per sprig. Twelve further samples of cress were examined, with the following results:—The bacterial counts per sprig (agar, 48 hours at 22° C.) ranged from 1,080,000 to 50,000,000, whilst, after washing, the counts ranged from 42,000 to 2,200,000. The coli-aerogenes organisms (48 hours at 37° C.), on samples other than the one forming the subject of complaint, ranged from 0 to 6 per sprig. Traces of duckweed were present in the samples more often than not, and some supplies contained many fresh water animals, including snails, *Gammarus pulex*, and small fish. Most of this extraneous matter could be removed by washing.

The regulations for watercress sold under National Mark designation require the cress "to be clean, well favoured, fresh, in good condition, free from woody or long stalks, seed or flower stems, pointed leaves or long roots, free from damage caused by frost, insects, disease, mechanical or other means." The beds are to be "so designed as reasonably to prevent contamination, infiltration or drainage of surface water," while the water entering the beds must be of the same degree of purity as required for drinking water supply.

Apart from these regulations, there appear to be no standards for watercress. Experience in this laboratory indicates that even the worst samples are rendered sufficiently clean after thorough washing, and a standard of ten *B. coli* per three-gram sprig on the unwashed samples appeared to be reasonable enough to include most commercial samples.

F. C. BULLOCK

METROPOLITAN BOROUGH OF HAMMERSMITH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1938

"TRIPLE CREAM CHEESE."—A sample sold under this name contained only 42 per cent. of fat and was reported adulterated. In my opinion it should have contained not less than 70 per cent., which is the standard for double cream cheese in the Agricultural Produce (Grading and Marking) Regulations (*cf.* ANALYST, 1939, 822). If grades higher than "double" are to be sold, a fat-standard higher than 70 per cent. would seem necessary. A cream (single cream) cheese subsequently examined contained 41·6 per cent. of fat.

Potato Starch in Flour.—A sample of ordinary flour contained 25 per cent. of potato starch and was reported adulterated. Two samples, sold as bun flour, also contained potato starch, but as I did not consider that objection could be taken to an admixture sold under this name, they were reported genuine.

"Vinegar Acid."—This was found to be a solution of acetic acid of 31·7 per cent. strength; that is, it was nothing more than the ordinary acetic acid of commerce. It is questionable if the sale of this article as a food adjunct is really safe. Two deaths through the injudicious use of it are mentioned in the 1936 Annual Report of the Chief Medical Officer of the Ministry of Health, and in the tropics cases of suicide and murder have been attributed to it. F. W. Edwards

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ALLEGED POISONING OF CATTLE BY PRUSSIC ACID IN LINSEED CAKE

In March, 1939, an action was brought in the Kilmarnock Sheriff Court by Thomas Drummond, farmer, against A. Patterson & Sons, grain and hay merchants, of Kilmarnock, for payment of £419 11s. 3d. in respect of alleged loss and damage to his cattle through using feeding stuffs supplied by the defenders, and in particular linseed cake alleged to contain substances capable of yielding hydrocyanic acid. The defenders denied pursuer's averments and alleged that the pasture in the pursuer's field was poor in quality and contained buttercups and other weeds that were poisonous and injurious to cattle.

Mr. Drummond stated that he purchased a quantity of linseed cake, maize, and sheep and lamb cake and, after mixing them in equal proportions, fed 20 calves. These calves scoured badly, but after the feed had been stopped they recovered in about 10 days. One heifer which refused to eat the mixture was not affected. Four bulls and nine heifers continuing to be fed became worse. One bull staggered about and its condition looked hopeless. It was slaughtered, and when it was opened the heart was still beating. The mixture had been fed dry to the animals. He denied that there was an undue proportion of buttercups in the field.

Mr. R. M'Dill Smith, veterinary surgeon, stated that when he examined the animals he thought they were suffering from prussic acid poisoning and suspected the linseed cake. When the bull was killed and opened the heart was still beating. After breathing had stopped the heart beat for three minutes, and that, together with the cherry-red blood coloration, was a symptom of prussic acid poisoning.

Professor J. R. M'Call, West of Scotland Agricultural College, said that the high arterial colour of the blood of the animal that was slaughtered, and the fact that the heart continued to beat after breathing stopped, were two of the typical signs of prussic acid poisoning.

Mr. J. R. Nicholls stated that his analysis of the portion of the sample submitted to the Government Chemist showed that the linseed cake contained cyanogenetic glycosides capable of yielding 3·85 grains of hydrocyanic acid per pound. This quantity was yielded after digestion with cold water for either two hours or eighteen hours and was potentially dangerous to cattle if fed to the animals in a way which allowed of the development of this hydrocyanic acid. The amount was high, but it was not abnormal. He did not know of any case in which linseed cake fed dry had produced harmful results. There would be more chance of harmful results if it was fed after soaking, but the presence of sugars and vegetation obtained during grazing would reduce the potential effect.

Mr. William Millar, analytical chemist, Greenock, said that he had had samples of linseed cake which had no potential prussic acid yield and he had also had a sample which yielded 7 grains per pound. He found starch in the linseed cake, and that suggested to him that it was cake made from seed which was not fully ripened. In his opinion the quantity of 3·85 grains per pound found by the Government Chemist was excessive.

Mr. J. G. Gordon, veterinary surgeon, Galston, gave evidence regarding three cases in his experience of suspected prussic acid poisoning from linseed cake which he had been informed was fed dry.

Mr. R. Laird, Agricultural Organiser for Ayrshire, stated that there was nothing in the herbage that, in his opinion, was likely to injure calves.

At the resumed hearing on May 8th evidence was given on behalf of the defenders. Mr. A. B. Shepherd said that for 30 years he had been chief chemist to the British Oil and Cake Mills, Ltd. It would be true to say that almost every linseed cake was capable of developing hydrocyanic acid. He had tested samples of the cake supplied to the pursuer and found it to yield 4·1 grains of prussic acid per lb.; this was not abnormal in any way. Apart from very exceptional cases, he had never obtained less than 3 grains of prussic acid per lb. from linseed cake manufactured from Indian seed, and he frequently obtained more than 4 grains per lb. He could not imagine normal animals being poisoned if they consumed, in a dry state, linseed cake with a potential yield of 4·1 grains of prussic acid per lb. If the cake were fed wet to young calves without being boiled, that would be a different matter, because the prussic acid would be actually developed.

Mr. H. Gillmore, veterinary surgeon, said that he visited the farm of Thomas Drummond to report on a case of illness in calves. He did not see any symptom of prussic acid poisoning in the animals. At the post-mortem examination of a slaughtered bull calf's internal organs a slight inflammation of the fourth stomach and intestinal tract was found. That was consistent with an irritant, and the commonest irritant was a parasitic infection. In his opinion, the suggestion that this animal showed symptoms of prussic acid poisoning three weeks after its last feed of linseed cake was ridiculous.

Professor W. Christopher Miller, of the Royal Veterinary College, London, said that, in his opinion, the animals were not poisoned by prussic acid generated by linseed cake. Whatever Mr. Drummond's calves had suffered from, it appeared to have been of a chronic character. Witness had never heard it suggested before that prussic acid in sub-lethal doses could produce a chronic condition.

Professor William Robb, of the Glasgow Veterinary College, said that if the animals in this case had a sub-lethal dose of prussic acid at every feed he would expect the symptoms to manifest themselves immediately, but they would recover in half-an-hour or an hour. This was the first case on record where it was alleged that the symptoms manifested had become chronic and long continued. He had never known an illness to follow the dry feeding of linseed cake and other foodstuffs with a potential yield of prussic acid. It should be well known among farmers that linseed cake, fed wet, might produce prussic acid poisoning. Prussic acid was not an irritant or corrosive poison. The condition of the intestinal tract of the animal that was slaughtered was consistent with gastro-enteritis, and that condition could be produced by plant poisoning if long continued.

Dr. D. G. O'Brien, of the West of Scotland Agricultural College, Auchincruive, said that buttercups were a recognised source of plant poisoning among livestock. The affected animal would not recover very quickly, because buttercup poisoning had a cumulative effect.

At the adjourned hearing of the case on September 14th, Sheriff Martin Laing gave his decision. He found it admitted or proved that the linseed cake supplied by the defenders contained cyanogenetic glycosides capable of yielding 3·85 grains of hydrocyanic acid per lb.; that such a potential content of hydrocyanic acid was not abnormal, and that such cake, if fed to animals in the recognised way and amount, was not injurious to them. His Lordship also found that the pursuer had not proved:—(1) that the linseed cake supplied to him by the defenders had an abnormally potential high rate of yield of prussic acid; (2) that scouring or persistent scouring was a symptom of prussic acid poisoning; (3) that feeds of ⅓ lb. of cake with a potential yield of 3·85 grains of prussic acid per lb., given twice daily to calves in the usual manner, and where the other articles of food, such as cooked maize and sheep and lamb cake, as well as vegetation obtained by the animals while grazing, were capable of impairing the functions of the animals so as to result in chronic prussic acid poisoning or chronic and permanent scouring; (4) that the illness from which the cattle suffered was due to the cake supplied by the defender to the pursuer, or that it was unsuitable as such.

The first official sample of cake for analysis was taken on September 14th, 1938, and his Lordship found in fact and in law that the delivery of the cake to the pursuer in sacks having stencilled on each the contents of linseed cake required to be stated by the manufacturers, constituted a delivery in writing of the statutory statement by the defenders to the pursuer on August 12th, and that, the first official sample for analysis not having been taken within 14 days from such delivery, the pursuer had not complied with the requirements of the Statute so as to enable him to have the benefit of the statutory warranty that the goods were to be in all respects suitable for feeding to cattle.

His Lordship found in law: (1) that the pursuer having instructed defenders to supply him with linseed cake of a particular trade name, and the defenders having supplied him with such cake, there was no breach of the implied warranty in the Sale of Goods Act, 1893; (2) that the pursuer having failed to prove that the illness from which his cattle suffered was due to the linseed cake supplied by the defenders, or to its being unsuitable as such, the defenders were not in breach of the implied warranty in terms of the Fertilisers and Feeding Stuffs Act, 1926, Sec. 2.

The Sheriff assoilzied the defenders from the conclusion of the action, and found the pursuer liable to the defenders in the expenses.

Ministry of Health

Public Health (Preservatives &c. in Food) Amendment Regulations, 1939

PROVISIONAL RULES AND ORDERS, 1939*

PROVISIONAL REGULATIONS, DATED OCTOBER 20, 1939, MADE BY THE MINISTER OF HEALTH UNDER THE FOOD AND DRUGS ACT, 1938 (1 & 2, GEO. 6, c. 56)

THE Minister of Health, after consultation with the Minister of Food, has made Regulations to Amend the Public Health (Preservatives, &c., in Food) Regulations, 1925–1927, to come into force on the date thereof (October 20, 1939).

The Public Health (Preservatives, &c., in Food) Regulations, 1925, as amended shall be further amended as follows:

(1) The following additional proviso shall be inserted at the end of Article 4 (1) and at the end of Article 11 (1).

> "(iv) The provisions of this Article shall not apply so as to prohibit the presence of added sodium or potassium nitrite in bacon, ham and cooked pickled meat."

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* **H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 1d. net.**

(2) The following paragraph shall be inserted after Article 4 (3):

"No person shall manufacture for sale or sell any cooked pickled meat, other than bacon and ham, which contains sodium or potassium nitrite in proportions exceeding two hundred parts per million calculated as sodium nitrite."

(3) The following paragraph shall be inserted after Article 11 (2):

"No person shall import into England or Wales any cooked pickled meat, other than bacon and ham, which contains sodium or potassium nitrite in proportions exceeding two hundred parts per million calculated as sodium nitrite."

Department of Scientific and Industrial Research

FOOD INVESTIGATION

FRUIT PECTINS: THEIR CHEMICAL BEHAVIOUR AND JELLYING PROPERTIES*

This report is based on work carried out during a period of several years by members of the staff of the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades, under the guidance of Mr. T. Macara, F.I.C., and the more immediate direction of Mr. C. L. Hinton, F.I.C., who has prepared the report for publication.

The report begins with an introduction and a survey of present knowledge of the constitution of pectins, and then proceeds to discuss the methods available for their characterisation. A study of the variations in the chemical properties of pectins, as extracted from fruits, is made the basis for an eventual explanation of their jelly-forming behaviour. As a criterion for true jelly-forming pectin a first approximation is the substance precipitated from fruit extracts by weak alcohol or acetone and separated from contaminating matter by re-solution and re-precipitation. For a more exact characterisation it is shown that the yield of calcium pectate is satisfactory. This criterion, however, cannot be applied with exactness directly to fruit juices and extracts; with such products the pectin should be separated by a preliminary precipitation with alcohol or acetone prior to the determination of the calcium pectate.

Measurement of Jelly-forming Capacity.—In comparing the jelly-forming capacities of different pectins the term "jellying power" is used. This is taken to be the strength of a jelly given by a pectin (as defined on the basis of calcium pectate yield) under standard conditions. The jellies were prepared by mixing 35 parts of pectin solution with 65 parts of glycerin at 70° C., and the mixtures were poured into tins or boxes, which were placed in an ice-chest for 24 hours before the test. It was found that the jellying powers were best compared at a *p*H of 2, and that a concentration of 0·35 per cent. of pectin (as calcium pectate) gave a satisfactory range of strengths for comparing various grades.

Chemical Properties.—A study was made of the chemical properties of a number of pectins prepared from fruits by different procedures and purified by re-solution and re-precipitation with weak alcohol or acetone.

The free acidity, *p*H of the solution, and the proportion of alkaline ash constituents varied widely, but were related in such a way as to show that the alkaline ash constituents were derived from metallic bases united with acidic groups of the pectin. The composition of the extracted pectin as regards these properties depended upon various treatments during preparation, which tended to remove or increase the amount of the basic constituents.

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* Special Report No. 48. Pp. 96. H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 1s. 6d. net.

The methoxyl-content also varied considerably with the method of preparation, and the proportion of total acidic groups also showed some, though less, variation. It being accepted that the constituent units of the pectin molecule are mainly galacturonic acid, the results showed that the proportion of such units ranged from 75 to 95 per cent. of the whole. The irregularity of the variations suggests that the carboxyl-content of a pectin is an average for a variety of differently carboxylated molecules.

The reducing power towards alkaline iodine solution varied irregularly, and in some of the preparations may have been due to non-pectin material.

Having regard to the differences in the properties of the specimens prepared, it is claimed that "pectin" must be regarded as a generic term covering a wide range of minor variations in molecular composition.

Effect of Heating on the Properties of Pectins.—Boiling the aqueous solutions of pectins caused a rapid loss of jellying power and, inversely proportional to it, an increase of iodine-reducing power. This suggests that deterioration by boiling is due to the cleavage of long-chain molecules by hydrolysis. No significant changes in other properties were observed after one hour's boiling. At 80° C. the loss in the jellying power of pectin solutions was smaller than at the boiling-point.

Action of Pectase on Pectins.—Considerable losses of available pectin in fruits and unheated fruit juices may be caused by the pectase partly de-esterifying the pectin, which is then, in part, converted into a relatively insoluble calcium salt. Whilst the loss of methyl alcohol does not alter the jellying power to a significant extent, yet it may affect the degree to which that power is available under normal *p*H conditions. This may explain the discordant views that have been published as to the relation between methoxyl-content and jellying properties.

Effects of Alkalis and Acids.—The question of the effect of moderate amounts of alkali short of complete neutralisation merges into that of the effects of salts and of *p*H conditions. At the ordinary temperature rather strong acid appears to have a beneficial effect upon the jellying power. Thus a pectin precipitated from an extract approximately $N/2$ in HCl produced a stronger jelly than one precipitated from an extract approximately $N/20$ in HCl. The free acidity (as NaOH per cent. of calcium pectate yield) of the former was 5·7, and that of the latter 3·9. The rates of de-esterification in $N/20$ hydrochloric acid at various temperatures, and in boiling water, were determined. The results indicated that a loss of methyl alcohol sufficient to modify the jellying properties appreciably is not likely to occur under practical conditions (apart from enzymic action) except in the extraction of pectin from citrus peel or fruit with hydrochloric acid.

The rates of hydrolysis in presence of hydrochloric acid were measured by determining the increases in iodine-reducing power. Pectins were found to be relatively resistant to hydrolysis in this way, though even a small degree of hydrolysis could be accompanied by a considerable loss in jellying power.

Effects of Salts.—It was found that pectins could take up calcium from solutions of calcium salts, and that the resulting calcium pectates had improved jellying properties. This probably applies also to other metallic salts, and it is suggested that acids (and moderate amounts of alkali) modify the strength of jelly obtainable from a pectin or pectinous solution by regulating the extent to which this interaction with metallic salts occurs. For the study of their jelly-forming properties pectins must be regarded as complex carboxylic acids of variable composition.

Factors Modifying Jelly-forming Properties.—Allowance being made for the effects of the treatments during preparation, the initial jellying powers of the pectins in the various fruits covered a wide range, and there was some variation even in the pectins of a single kind of fruit. The methoxyl-content, however, must have varied much less prior to extraction of the pectin, provided that there had been no opportunity for pectase action; in most instances its amount was from 11 to 12 per cent.

The factors discussed and finally summarised in the report indicate that the jellying power of a pectin (as distinct from the strength of the jellies it gives under conditions of use) is controlled by: (*a*) its inherent quality (*i.e.* some pectins, *e.g.* that of strawberries, are naturally weak; others, *e.g.* those of citrus fruits, naturally strong); (*b*) the degree of heating to which it has been subjected; (*c*) the possibly beneficial effect of acid treatment at ordinary temperatures; (*d*) the degree of de-esterification caused by acids or pectase action; (*e*) *p*H conditions, as fixed by the buffering constituents of the fruit juice, or, with pure pectin solutions, by the extent to which the free acidity of the pectin is neutralised; (*f*) the apparently beneficial effect of some salts in modifying salt formation by the pectin itself.

BIBLIOGRAPHY.—The Report concludes with an alphabetical list containing 45 references relating to the composition, properties and methods of determining pectins.

THE SOLUBILITY OF CEMENTS*

AN investigation on methods for comparing the relative resistance of cements to leaching when soft waters percolate through concrete has been carried out at the Building Research Station. The investigation was undertaken at the instance of the Joint Sub-Committee on Special Cements nominated by the Institution of Civil Engineers and the British Committee on Large Dams, who have had under consideration the properties desirable in cements to be used for mass concrete subjected to water pressure, on one side.

The solubility of cement is recognised as one factor to be considered in the deterioration of concrete dams exposed to the action of pure and slightly acid natural waters. It is commonly observed that in dams that have become leaky a deposit of lime is found on the down-stream face. While the primary cause of deterioration is the permeability of the concrete, the extraction of the lime from the cement and its removal in solution must eventually increase the rate of decay. When the water impounded behind a dam is hard the amount of leaching is not usually serious, and, indeed, lime may even be deposited from the water rather than removed by it in solution. With soft waters, however, such as are common in many mountain areas, solution of the lime may become a serious factor, and many instances of decay of this type have been reported abroad.

EXPERIMENTAL METHODS.—The methods, described in the Report, that have been studied for comparing the solubilities of set cements may be divided into three main classes: (1) Extraction tests on set cement; (2) percolation tests on mortars and concretes; (3) surface solution tests on mortars and concretes.

(1) *Extraction Tests.*—In these methods the set or neat cement, after being cured in water for the time desired, is crushed to a given size and extracted with water under specified conditions. The amount of lime dissolved is taken as a measure of the relative solubility. Three variations of this method have been described by Swedish investigators. The method used in the present tests was that of the Swedish Cement Laboratory (Werner, *Zement*, 1931, **20**, 626).

Cubes (50 cm. faces) made of neat cement, gauged with 28 per cent. of water by weight, were cured for 3 days in moist air at 18° C. and then in water at 18° C. until 1 or 3 months old. The set cement was then crushed, and a fraction of grain size 0·21–0·09 mm. (British Standard sieves, Nos. 72 and 170) was used for the test. A 1-gram sample was then extracted with 15 successive volumes (20 ml. each) of distilled water, the filtrates from each five successive extractions were combined, and the lime in solution was determined. The loss on ignition of the set cement was determined, and the total amount of lime was calculated as grams of CaO per g. of anhydrous cement.

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* Building Research Paper, No. 26. H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 6d. net.

(2) *Percolation Tests.*—These methods involve the collection of water which has percolated through mortar or concrete test specimens, and the determination, in this water, of the lime extracted from the cements. Such tests are usually made under high water pressure.

(3) *Surface Solution Tests on Mortars and Concretes.*—In this method, as developed by Rengade (*Rev. Matér. Constr.*, 1932 [275], 309; [276], 363), specimens of mortar (1:3) are subjected to the action of a jet of water impinging on their surface. The extent of wear or erosion is used as a measure of the relative solubility of cements.

Tests with these various methods were made on two normal Portland cements, two Portland blast-furnace cements and one pozzolanic cement. From the results the conclusions were drawn that concrete percolation tests do not entirely simulate practical conditions. Percolation tests on lean mortars through which water can be passed at relatively low pressures are simpler in technique, but the results are not satisfactory. The Swedish method is simple in operation and the reproducibility of the results is good. Since, however, the test involves the crushing of the set material, with partial destruction of its physical structure, it seemed uncertain if it would correctly indicate the relative behaviour of cements when used in concrete. The method developed by Rengade is simple in operation, but it involves a mechanical erosive action in addition to a solvent action. According to Rengade, however, the mechanical erosive action does not actually play an important part in this test, since if hard waters of low solvent power are used, no erosion occurs. The test is qualitative and requires a rather prolonged period of time. It is also a test of the surface of the material and, though its results give a good indication of the relative resistances of concretes, made with different types of cement, to surface erosion when exposed to running water, it is more doubtful if this applies to conditions where percolation through the concrete mass has occurred.

Although the Swedish extraction method cannot reproduce quantitatively the differences found between cements in the concrete tests, it suffices to place them in a relative order which seems adequate for practical purposes. Its use is therefore recommended, but no significance should be attached to small differences in the results it yields. It should show satisfactorily whether a cement of the pozzolanic or blast-furnace type offers much more pronounced resistance than Portland cement to leaching of lime.

Determination of Extracted Lime.—In the volumetric method for determining the lime-content of the solutions collected in the various tests, the mixed methyl red and bromothymol blue indicator (described below) was used. This indicator was added to the solution in the proportion of 10 ml. per litre, and *N* hydrochloric acid was run in until the solution became red; 1 ml. of acid in excess was added, and the solution was shaken and allowed to stand to dissolve any alumina or calcium carbonate. If the yellow colour returned, a further 1 ml. of acid was added. The solution was then made up to a known volume, and a 25-ml. sample was taken for analysis. This sample was boiled for 5 minutes to expel carbon dioxide, cooled and back-titrated with *N*/10 barium hydroxide solution until the colour changed from yellow to green.

The mixed indicator was prepared by dissolving 0·4 g. of bromothymol blue in 1 litre of water and adding 0·5 g. of methyl red to the solution, which was then boiled, cooled and decanted. With this mixed indicator two colour changes occur on acidifying—from green to yellow at *p*H 7·0 to 6·5 and from yellow to red at *p*H 5·0 to 4·0. The addition of standard hydrochloric acid to a lime solution in presence of calcium aluminates, or of calcium carbonate, until a red colour persists, ensures that all alumina or carbonate is dissolved. If this acidified solution is then titrated back with standard alkali, to the yellow-green point, all alumina will be re-precipitated, and the difference between the two titres gives the total lime present as hydroxide, carbonate or aluminate in the original solution.

The total CaO content of the original solution is calculated as follows:

$$\text{Total CaO} = (A)\,(E_A) - B\left(\frac{V}{25}\right)E_B$$

where A represents ml. of acid added to the bulk solution; B, the number of ml. of baryta solution used in back-titration of 25-ml. samples; E_A, the equivalent of acid solution in g. of CaO per ml.; E_B the equivalent of baryta solution in g. of CaO per ml.; V, the total volume of solution from which the 25-ml. sample was taken.

International Union of Chemistry

FOURTH REPORT OF THE COMMITTEE ON ATOMS*

THE Committee recommend the following changes in the International Table of Stable Isotopes for 1939:

SULPHUR.—The work of Nier provides more accurate measurements of abundance for this element and suggests the presence of a new rare isotope 36.

CHLORINE.—The electrical measurements of abundance (Nier and Hanson) are adopted.

CALCIUM, TITANIUM.—The abundances are revised in accordance with the work of Nier, who has discovered two new isotopes of calcium 46 and 48.

ZINC, STRONTIUM, CADMIUM, BARIUM.—Nier's percentages are adopted; most of the changes are small.

GADOLINIUM, DYSPROSIUM, ERBIUM, YTTERBIUM.—In each of these elements new rare isotopes of low mass number have been discovered by Dempster and their abundances estimated.

LUTECIUM.—The heavier isotope suggested by the atomic weight and optical spectra has now been identified to be of mass number 176.

THALLIUM.—Nier's new ratio 0·410 for the relative abundances of the two isotopes is adopted.

PERMANENT COMMISSION ON THERMOCHEMISTRY

SECOND APPENDIX TO THE FIRST REPORT*

SUCCINIC acid was adopted as a secondary standard substance in 1934, at Lucerne, and its heat of combustion was provisionally fixed (3025·5 cal/g. at 20° C.). Further precision work, since published, has confirmed the provisional value.

For benzoic acid the value 6319 cal/g. at 20° C. (*in vacuo* for Washburn conditions) was adopted in 1934; also provisionally. In the meantime a further study of benzoic acid has been made at the Bureau of Standards, and a result 0·03 to 0·04 per cent. smaller than before has been obtained. Nevertheless the value 6319 cal/g., accepted until now, has been preserved; also, a table is now given, in which are recorded not only the heat of combustion of succinic acid, referred to the value hitherto accepted for benzoic acid (at 15° to 30° C.), but also the ratio between the increases in temperature per g. of benzoic acid/succinic acid.

The final values for the heats of combustion of the two substances have still to be settled. It is hoped that an agreement, binding on all, will soon be reached. With that end in view a proposal has been published and is to be submitted for discussion.

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* Published by the Secrétariat Général, 28, Rue Saint-Dominique, Paris. 1939.

British Standards Institution

THE following revised specification has been issued:*

No. 210—1939. British Standard Classification of Lubricating Oils

The Classification of Pure Mineral Oils (issued in 1924 and first revised in 1938) is intended to be a broad guide to users of lubricating oils, but not to provide detailed specifications for individual oils.

The basis of this Classification is viscosity in seconds (Redwood No. 1) at 140° F., except for Group 5, for which 200° F. is customary. For convenience, the corresponding units of kinematic viscosity in centistokes (cS) are also given.

All tests except viscosity have been omitted for the reasons indicated in the following notes on the significance of tests:

Demulsification.—This test measures the propensity of an oil to separate from water under standard conditions. The result bears no direct relation to other properties and is significant only for certain applications.

Pour-point.—This affords an indication of the temperature at which the oil ceases to flow under standard conditions. It does not follow that the oil will flow, under particular conditions of storage and use, above the pour-point.

Flash-point.—The flash-point is not necessarily an indication of the quality of a lubricating oil, but an abnormally low figure will indicate contamination by volatile products.

Oxidation Test.—There is as yet no generally accepted standard oxidation test for lubricating oils other than the sludge test in B.S. 489 (Turbine Oils), the correlation between oxidation tests and service behaviour being still incomplete.

Carbon Residue.—There are two carbon residue tests: the Conradson Carbon Test and the Ramsbottom Coke Test. Whilst these two tests are not inter-related, their indications are, in general, similar. The correlation between the carbon residue test and service results is still imperfect.

Acidity.—Lubricating oils should be free from mineral acid. The permissible limit for free organic acid depends entirely upon the application.

Asphaltenes (Hard Asphalt).—All pale oils and most red oils are free from hard asphalt. Black and dark cylinder oils usually contain varying percentages of asphalt. Limits for the hard asphalt content in such oils vary widely, dependent upon the service for which the oils are intended.

CLASSIFICATION.—It is intended that from this classification of lubricating oils according to their viscosity specifications may be developed by the addition of other physical or chemical characteristics. Each of the five main groups is sub-divided (as commercially practised) into viscosity grades under the names "Light," "Medium," "Heavy," etc., and limiting figures are given.

Group 1.—These lubricating oils have special qualities of separation from water and resistance to sludge and acid formation. Oils of this group are intended for use in engines such as turbines and high-speed enclosed crank chamber steam engines where lubrication is by pump circulation.

Group 2.—Lubricating oils in this category are intended, according to grade, for lubrication of bearings (such as motors, dynamos) and closed crank case steam engines, etc., where conditions are similar to Group 1 but less exacting.

Group 3.—Lubricating oils suitable for use where working conditions tending to deteriorate the oil are not severe, such as for shafting, bearings, axles, etc., and other systems where lubrication is not by pump circulation, temperatures are not high and water is not present.

Group 4.—Internal combustion engine oils.

Group 5.—Heavy lubricating oils for use in gears, bearings, steam engine cylinders, etc.

LIST OF BRITISH STANDARD SPECIFICATIONS (A.R.P. SERIES) AVAILABLE FOR CIVIL DEFENCE PURPOSES†

The Home Office Air Raid Precautions Department has authorised the British Standards Institution to prepare and issue on their behalf a special A.R.P. series of British Standard Codes, Specifications and Schedules for Materials or Appliances required for Air Raid Precaution purposes.

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* Publications Department, 28, Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

† Copies of the Specifications 1 to 20 can be obtained from the offices of the British Standards Institution, 28, Victoria Street, London, S.W.1, price 3d. each, post free.

The following Specifications have been published:

B.S./A.R.P. 1. Aggregates for Concrete Shelters Constructed *in situ*.
2. Bituminous Paint and Bituminous Compound for the Protection of Steelwork.
3. Electric Hand-lamps (fitted with primary battery or unspillable accumulator).
4. Apparatus for Decontamination of Oilskin Clothing.
5. Chemical Closets for Use in Shelter Accommodation.
6. Shelter Lighting (shelters for 50 persons [210 sq. ft.] or multiples thereof up to 200 persons).
10. Rubber Gaskets for Rendering Doors and Windows Gas-tight.
11. Adhesive Tape for Fixing Gas-proof Material, Repairing Damaged Material or Sealing Apertures and Cracks, etc.
12. Petroleum Jelly for Sealing Gas-tight Doors, etc.
14. Black Blind Material for Obscuring Windows.
15. Light Traps for Shops.
16. Specific Methods of Providing Even Illumination of Low Intensity (0·002).
20. Specific Methods of Providing Even Illumination of Low Intensity (0·02).

The following Specifications are in course of preparation and will shortly be published:

Electric Lighting of Control and Report Centres.
Wire Netting for Protection against Flying Glass from Roof Lights and Windows.
Blanket Felt for Rendering Doors and Windows Gas-proof and Forming Gas Locks.
Electric Lighting of Air Raid Shelters (large).
Fluorescent Paints.
Adjustable Hinges.
Specific Methods of Providing Even Illumination of Low Intensity (0·2).
Blind and Curtain Material (Textile).
Gas-proof Cloth for Rendering Windows Gas-proof and Weatherproof after Breakage.
Mixture for Anti-gas Cloth.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Composition of Goats' Milk of Known Purity. H. C. Lythgoe. (*Amer. Chem. Soc., Div. Agric. Food Chem., Meeting,* Sept., 1939, *Absts.*, 7.)—Samples of goats' milk were collected from individual goats and 9 samples from a herd from December to July, and analysed. Solids, fat, solids-not-fat, lactose, protein, casein, ash, freezing-point, copper serum refraction, acetic serum ash, and in a few instances calcium-content were determined. On the whole, solids, fat and ash were higher than in cows' milk for December and March, but in May, June and July solids and fat dropped considerably, ash remaining high. The season appeared to have a greater influence than the stage of lactation. The protein-fat ratio is of little value for goats' milk owing to the extreme variation, and the same remark applies, but to a less extent, to the serum figures, so that skimming and watering are at present less liable to detection than with cows' milk. Although the proportion of calcium in the acetic serum ash is much the same as for cows' milk, the higher ash-content causes the amount of calcium per quart to be higher. Less phosphatase is present and it is destroyed at 142° F. in 10 to 15 minutes, so that this test has little value in detecting improper pasteurisation of goats' milk.

D. G. H.

Report on the Use of Devices called "Meat Softeners." A. Besson. (*Ann. Falsificat.*, **1939, 32,** 260–263.)—Meat softeners are implements which make meat tender by penetrating it deeply in a series of fine parallel perforations. The interior of the meat is therefore deeply inoculated with microbes, from the air and from the softener, some of which may cause putrefaction of the meat, while if others, of the salmonella group, are present, toxins are formed which may cause food poisoning. As the internal temperature of roasted or grilled meat is seldom high enough to destroy these bacteria and toxins, the risk is greatest from meat cooked in these ways. Since February 7, 1930, French butchers have been advised to discontinue the use of softeners, and on December 7, 1936, the manufacture, sale and putting on sale, and the use of such articles in all places where raw or cooked meat is delivered to the public, were forbidden by a French statute. On February 14, 1938, this prohibition was confirmed and extended to the whole country in so far as the manufacture, sale and use of meat softeners were concerned. E. B. D.

Canned Atlantic Crab. A New American Food. C. B. Fellers and S. G. Harris. (*Amer. Chem. Soc., Div. Agric. Food Chem., Meeting*, Sept., **1939**, *Absts.*, 6.)—The live blue crab (*Callinectes sapidus*) is steamed and eviscerated, and the meat is hand-picked and dipped in a protective brine, which contains, besides sodium chloride, small amounts of aluminium salts and lactic acid. After draining it is packed in parchment-lined cans, sealed under high vacuum, and heated at 250° F. for 30 minutes. By this method the characteristic colour and flavour are retained. The crab's blood contains 60 p.p.m. of copper and the flesh 2 to 6 p.p.m., and this accounts for the discoloration in untreated crab meat. The reduced form of haemocyanin is, however, colourless. Blue to black copper ammonia complexes may also form, as ammonia is liberated by heat from the crab protein, but the protective action of aluminium and zinc salts is found to be quantitative, consistent and permanent. Aluminium is preferred to other possible metallic salts from a health point of view. D. G. H.

Composition and Food Value of Wild Rice (*Zizania aquatica.* L.). J. A. Le Clerc, R. G. Capen and C. E. Chambliss. (*Amer. Chem. Soc., Div. Agric. Food Chem., Meeting*, Sept., 1939, *Absts.*, 6.)—About 40 authentic samples of wild rice, grown chiefly in northern Minnesota, have been analysed. The percentage composition of the hull-free seed was as follows:—moisture, 8·8 to 10·0; fat, 0·5 to 1·05; sugars, 2·20 to 3·7; pentosans, 1·6 to 2·1; protein, 13·0 to 17·0; fibre, 0·90 to 1·35; calcium, 0·02 to 0·03; magnesium, 0·11 to 0·19; potassium, 0·27 to 0·39; phosphorus, 0·32 to 0·42; sulphur, 0·05 to 0·07; chlorine, 0·01 to 0·02. The weight of 1000 kernels varied from 27 to 35 g. and the percentage of hulls from 15 to 21. Parched and mature seed both showed rather lower figures than the natural and immature seed, respectively. D. G. H.

Glycogen in the Seed of Maize (variety Golden Bantam). D. L. Morris and C. T. Morris. (*J. Biol. Chem.*, 1939, **130**, 535–544.)—The observation previously made that the crystallisation pattern of cupric chloride in presence of an extract of the seeds of maize was similar to that obtained in presence of a glycogen solution, and different from that obtained in presence of a dextrin solution, led the authors to suggest that the complex polysaccharide present in *Zea mays* is not a dextrin, as has long been supposed, but glycogen. The physical and chemical properties of the polysaccharide are very similar to those of both glycogen and erythrodextrin. For example, it was quantitatively hydrolysed to glucose by means of dilute acid, it was extremely resistant to the action of hot 60 per cent. potassium hydroxide solution, $[\alpha]_D$ was equal to +187°, and $[\alpha]_D$ for a pyridine solution of its triacetyl derivative was equal to +158°. Measurements of the rate of hydrolysis with malt diastase, however, showed that the corn polysaccharide was hydrolysed at almost the same rate as yeast glycogen, oyster glycogen and liver glycogen, whereas dextrin was hydrolysed much more rapidly. This evidence is regarded as establishing, first the identity of the polysaccharide with glycogen, and secondly, the validity of the cupric chloride crystallisation patterns as criteria for the identification of glycogen. (*Cf. J. Physical Chem.*, 1939, **43**, 623.) F. A. R.

Composition of Seeds of *Sapindus drummondii*. O. C. Dermer and L. T. Crews. (*J. Amer. Chem. Soc.*, 1939, **61**, 2697–2698.)—The drupe-like fruit (average weight of one = 1 g.) of the tree *Sapindus drummondii* H. and A., which is widely distributed in the south-western part of the U.S.A., contains a round black hard-shelled seed with an average weight of 0·4 g. The pericarp is rich in saponin, and the seeds are capable of taking a high polish. For the purpose of oil extraction the seeds were mostly ground whole, and the oil was obtained by extraction with ether or petroleum spirit and by pressure, but in each instance the resulting oil gave substantially the same constants. The seed kernels contained 42·7 per cent. of ether-soluble material, and the whole seeds 23 to 24 per cent. The greenish to yellow-brown oil had the following characteristics:—sp.gr. at 25/25° C., 0·903 to 0·917; n_D^{20}, 1·4704 to 1·4722; saponification value, 213 to 219; iodine value (Hanus), 81·5 to 83·5; Reichert-Meissl value, 0·0; Polenske value, 0·0; acetyl value, 14·5; thiocyanogen value, 63·9 to 67·2; unsaponifiable matter, 1·2 per cent.; acid value, 0·3 to 0·9; unsaturated acids, 74 to 77 per cent. (calculated from the iodine and thiocyanogen values), 82 per cent. (by separation, weighing and correcting for impurities); saturated acids by the same method, 17 to 20 and 13. Separation of the saturated acids was effected by low-temperature crystallisation from acetone. The fatty acids were found to consist chiefly of oleic acid with smaller quantities of stearic and palmitic acids. A small amount of alkanes (presumably from the seed-coat) was also found. The seed oils of the following relatives of *Sapindus drummondii* have been studied:—*Schleichera trijuga*, *Nephelium lappaceum*, *Nephelium mutabile*, *Sapindus trifoliatus*, *Ungnadia speciosa*, *Sapindus mukurossi* and *Sapindus marginatus*. The iodine value of the oil of *Sapindus drummondii* is higher than those of the others except in the case of *Sapindus marginatus*, but the chief point of difference appears to be in the lack of *n*-eicosanic (arachidic ?) acid in the oil of *Sapindus drummondii*. D. G. H.

Argan Oil. W. H. Dickart. (*Amer. J. Pharm.*, 1939, **3**, 293–294.)—The hard kernels of the plum-like drupes of the Marocco ironwood or argan tree give, on pressing, an oil having an odour of burnt almonds and a bland nutty flavour. The oil had the following characteristics:—sp.gr. at 25° C., 0·9160; solidif.pt., 24·8° C.; saponification value, 190·4; iodine value (Wijs), 96·4; acetyl value, 1·81; acid value, 3·0; free fatty acids (as oleic), 1·5 per cent.; unsaponifiable matter, 0·36 per cent.; Kreis test for rancidity, negative; Halphen test for cotton-seed oil, negative; Bellier test, positive; tea-seed oil test (modified Liebermann–Burckhard test), positive; arachis oil test (modified Renard–Tolman, U.S.P. method), gave an acid (but apparently not arachidic) m.p. 65·0° C. and iodine value, 21·7; colour (Lovibond 5¼″), 35 yellow, 7·4 red; nitric acid colour test, crimson; total fatty acids, 90·72 per cent. with m.p. 27·0° C. and iodine value, 99·7; saturated acids, 12·83 per cent. with m.p. 55·6° C.; unsaturated acids, 77·89 per cent. with iodine value 115·2; unidentified acid, 0·63 per cent. (see arachis oil test).

D. G. H.

Identification of Flavouring Constituents of Commercial Flavours. Determination of β-Ionone. J. B. Wilson. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 690–693.)—The method previously described (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 378) for the determination of quantities of β-ionone as low as 10 mg. has been successfully applied to commercial flavours containing 50 to 200 mg. of β-ionone per litre. Since precipitation of β-ionone-*m*-nitrobenzhydrazide does not occur readily in 10 ml. of dilute alcohol (1 + 1) unless 20 mg. or more are present, it is unnecessary to await the beginning of crystallisation before diluting the solution to an alcoholic content of 30 per cent. by volume. When 10 mg. or less are present, the hot solution of ionone and reagent may be diluted immediately and, after acidification, set aside for crystallisation, which begins within 30 minutes. The method is as follows:—A solution of the flavouring substance, containing 1 to 10 mg. of β-ionone in 5 ml. of alcohol, is treated with 90 to 95 mg. of solid *m*-nitrobenzhydrazide, and the mixture is warmed (without loss of alcohol) on a steam-bath. Warm water (10 ml.) is added, and, if the solution becomes cloudy, it is warmed until clear. It is then treated with 0·2 ml. of glacial acetic acid and the lightly stoppered flask is allowed to cool slowly. If 2 mg. or more of β-ionone are present, crystals begin to form within 30 minutes after the mixture has attained room temperature. The crystallising liquid is allowed to stand for at least two hours and is then placed in a refrigerator overnight or for a period not exceeding 48 hours, and is filtered through a sintered glass crucible with the aid of suction. The crystals are washed with 15 ml. of cold 30 per cent. alcohol and dried in a vacuum oven at 70° C. The weight of β-ionone is found by multiplying the weight of the precipitate by 0·541. To maintain the accuracy of the method when such small amounts are involved, it is recommended that ½-inch sintered glass plates should be made from Pyrex glass by the method of Kirk *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 154) and sealed into Pyrex tubing, which is then cut and fire-polished, so that crucibles, 3 cm. long, of 3 ml. capacity and weighing from 5 to 7 g., are formed with the disc about 1·5 cm. from the top. It was found that 1 mg. of material can easily be removed from the disc for microscopical identification. Directions are given for the construction of a suitable filter-flask, which can be used for filtration by suction through these crucibles. The accuracy of the method was proved by determining known amounts of β-ionone added to a commercial strawberry-flavoured dessert preparation. A. O. J.

Analysis of Powdered Red Peppers. Dumas. (*Ann. Falsificat.*, 1939, **32**, 247–250.)—Red pepper is obtained in Tunis by pulverising the whole fruit of *Capsicum annuum* after drying it in the sun for some weeks. Nine specimens from different regions and obtained in different years gave the following analytical percentage results:

Specimen	1	2	3	4	5	6	7	8	9
Moisture	10·41	10·81	8·89	9·19	11·58	13·07	6·79	10·75	9·49
Fixed oil	9·72	12·65	12·80	9·99	10·05	11·04	9·35	10·83	10·28
Volatile oil	0·36	0·39	0·37	0·37	0·35	0·16	0·36	0·33	0·17
Ash	6·58	5·87	6·61	5·80	5·91	6·93	6·40	6·17	6·99
Carbohydrates ..	8·70	12·30	11·05	11·40	12·85	10·42	14·40	14·23	12·33
Nitrogenous matter	15·75	15·75	16·63	17·50	16·65	14·88	14·25	15·40	15·31
Cellulose	20·65	21·86	23·22	21·35	22·95	23·55	24·50	23·80	23·78

All the samples of fixed oil obtained from these were deep red viscous liquids, with a very pungent odour and flavour; in filtered ultra-violet light they gave no fluorescence and appeared almost black; they dried very rapidly. Their constants, determined by the usual methods, were within the following range:—n_D^{20}, 1·4812–1·4836; iodine value, 131·9–141·6; acid value, 15·85–25·95; saponification value, 184–195; ester value, 164·40–173·25. The essential oils were of a very clear yellow colour and had a characteristic pungent odour. *Adulteration.*—Mineral matter and edible vegetable oil (*e.g.* olive or arachis oil) are the most frequent additions. The former is detected by the determination of the ash, while the high refractive index of the fatty matter is greatly lowered by addition of any vegetable oil; addition of 10 to 15 per cent. of olive oil has thus been detected. E. B. D.

Identification of the Barbiturates. R. F. Chatfield. (*Pharm. J.*, 1939, **143**, 346.)—The method of Paget and Tilly (*J. Pharm. Chim.*, 1937, **129**, 222; Abst., ANALYST, 1937, **62**, 399) for the identification of the barbiturates has been modified and extended to other barbituric acid derivatives. As before, 5 drops of Millon's reagent are added to a solution of 0·05 g. of the substance in 4 ml. of acetone. An instantaneous white precipitate, soluble on heating, indicates barbitone; insoluble, dial. Prominal causes slight opalescence immediately; this changes through turbidity (approx. 1½ minutes) to a heavy white precipitate (7½ minutes), which increases on heating but finally dissolves. Rutonal causes opalescence (1 to 2 minutes), which increases to a heavy turbidity (approx. 4 minutes), soluble on heating or on standing for approx. 8 minutes. Evipan, gardenal, phanodorm, amytal and soneryl, all of which cause immediate opalescence unaffected by heat, are identified by the addition of 5 drops of Millon's reagent to a solution of 0·05 g. of the substance in 4 ml. of 90 per cent. alcohol. A canary-yellow precipitate, insoluble on heating, which turns white on addition of one drop of conc. hydrochloric acid and dissolves to a colourless solution on boiling and adding 10 ml. of the acid, indicates evipan. A heavy white precipitate, insoluble on heating, soluble on addition of 10 ml. of conc. hydrochloric acid to the hot solution, indicates gardenal. Phanodorm, amytal and soneryl yield a white precipitate, wholly or partly soluble on boiling, and soluble on addition of 10 ml. of conc. hydrochloric acid to the hot liquid. The solution is pale yellow (phanodorm), colourless (soneryl) or cream-coloured and opalescent (amytal). In all the alcoholic solutions, addition of the acid produces first a heavy white precipitate and then an amber-coloured solution before the final reaction is obtained. A grey precipitate, which always appears finally in the acetone solutions (*cf.* Paget and Tilly, *loc. cit.*), is due to the decomposition of the reagent. E. B. D.

Biochemical

Deposition and Utilisation of Fatty Acids of Low Molecular Weight; and a Fatty Acid Analysis of Coconut Oil. H. E. Longenecker. (*J. Biol. Chem.*, 1939, 130, 167–177.)—Fasted male rats were fed on a ration in which coconut oil provided 84 per cent. of the calories. After 14 days, one group of rats was killed, and a second and third group were fasted until they had lost respectively 15 and 30 per cent. in weight and then killed. The total lipoid material was extracted from the carcases and the acetone-insoluble phospholipids removed. The acetone-soluble lipids were further analysed by methyl ester distillation. The proportion of major fatty acids per 100 g. of body weight found in the fats of the three different groups of animals is summarised in the following table:

		Fasted Groups			
		15 per cent. loss in body weight		30 per cent. loss in body weight	
Acid	Non-fasted group g.	g.	Per cent. utilised	g.	Per cent. utilised
Total acids.. ..	13·50	8·46	37·3	4·95	63·7
Lauric	3·60	1·69	53·1	0·92	74·4
Myristic	2·34	1·56	33·3	0·70	69·9
Palmitic	2·69	1·73	35·8	0·80	70·1
Oleic	3·21	2·63	19·1	1·73	46·2

The depot fat in the first group of animals had an iodine value of 31, as compared with 8 for the coconut oil. The increase in unsaturation may be the result of desaturation in the organism or preferential catabolism of the more saturated acids, or both. The iodine values of the fats from the rats that had lost 15 and 30 per cent. in weight were 36·9 and 40·0 respectively. It will be seen from the table above that the proportion of acids utilised during inanition was highest for lauric acid and lowest for oleic acid. This may be evidence of the preferential utilisation of saturated fatty acids of low molecular weight, but the results might also be explained by assuming the presence of dilaurins in the depot fat, and a maximum distribution of myristic, palmitic and oleic acids, with unselective removal of one glyceride molecule at a time from the depot fat. Dodecenoic acid and tetradecenoic acid were identified in the fat, and it therefore seems probable that the rat is able to desaturate lauric and myristic acids. F. A. R.

New Method for the Estimation of Uric Acid in Blood, with Uricase. M. B. Blauch and F. C. Koch. (*J. Biol. Chem.*, 1939, 130, 443–454.)—Many attempts have been made to improve the phosphotungstate colorimetric method for uric acid introduced by Folin and Denis (*J. Biol. Chem.*, 1912, 12, 239; 1912–13, 13, 469), but hitherto with only partial success. In the method now proposed, use is made of the specific action of uricase, so that the difference in colour before and after reaction with uricase is a true measure of the uric acid content. A tungstic acid filtrate of the blood to be tested is prepared by adding 2 ml. of 10 per cent. sodium tungstate solution to 2 ml. of the blood in a 50-ml. centrifuge tube, followed by 16 ml. of $N/12$ sulphuric acid, and centrifuging. A similar filtrate is prepared from the blood after treatment with uricase. Two ml. of the blood are incubated at 40° to 48° C. for 2 hours with 50 mg. of uricase powder. (This is prepared by dehydrating 1 lb. of minced, defatted, frozen beef kidney with four 500-ml. portions of acetone over a period of 48 hours at 4° C., 12 hours being allowed for each extraction. The tissue is dried at room temperature with the aid of a fan, and the dry material is treated twice with 500 ml. of benzene, the first treatment for 6 hours and the second for 12 hours. The extracted tissue is dried at room temperature, ground to 60-mesh size, and stored in a desiccator at 4° C.) The blood proteins and the uricase are then precipitated by adding 2 ml. of 10 per cent. sodium tungstate solution and 16 ml. of $N/12$ sulphuric acid. Duplicate 5-ml. samples of the filtrate from the uricase-treated blood and duplicate samples of from 1 to 5 ml. of the untreated blood filtrate are introduced into test-tubes. Standards, containing 1 to 5 ml. of a uric acid solution (0·005 mg. per ml.) in lithium carbonate solution preserved with formaldehyde are also prepared. The volume of the liquid in each tube is adjusted to 5 ml., and to each mixture are added, from a long-tipped micro-burette, 5 ml. of a freshly-prepared solution of 2·5 per cent. of sodium cyanide in 25 w./v. per cent. urea solution. One ml. of uric acid reagent is then added slowly from another similar burette. (This reagent is prepared by dissolving 100 g. of sodium tungstate in 700 ml. of water, adding 75 ml. of 85 per cent. phosphoric acid, and boiling the mixture gently under a reflux condenser for 24 hours. The solution is decolorised by adding a few drops of bromine or 30 per cent. hydrogen peroxide to the hot solution and boiling without the condenser for 10 minutes. The pale yellow liquid is diluted to 1 litre.) The contents of each tube are well mixed, and the tubes are stoppered and allowed to stand for 3 hours at room temperature, after which the colours of the unknown solutions are compared with those of the appropriate standards in a colorimeter. The apparent uric acid value obtained with the uricase-treated blood is subtracted from that of the untreated blood to obtain the true uric acid content. If, however, the colorimeter reading of an unknown solution differs appreciably from that of the standard, a correction has to be applied for the lack of proportionality between colour intensity and concentration of uric acid present. A table of corrections is given, but normally the maximum error is ± 5 per cent., and where readings differ greatly it is better to repeat the estimation with a more appropriate volume of filtrate.

The reliability of the new method was tested by recovery studies on pure uric acid solutions, and the errors were found to range from − 2·8 to + 5·1 per cent. The uric acid content of human blood (50 samples) was found to range from 1·04 to 3·83 mg. with an average of 2 mg. per 100 ml. The apparent uric acid content, obtained without uricase treatment, was 1·82 to 4·60 mg. with an average of 3 mg. per 100 ml. The difference, ranging from 0·60 to 1·54 mg., average 1 mg. per 100 ml., can be accounted for by the presence, in blood, of a number of other substances not affected by uricase, but forming a colour with the reagent. Uric acid added to blood was found to be quantitatively destroyed when incubated with uricase, leaving the same non-uric acid colour value as before. Recoveries of uric acid, added in quantities of 2 to 16 mg. per 100 ml. of blood, averaged 93·5 per cent. (16 samples). F. A. R.

Detection of Gold in Faeces. M. J. Schulte. (*Pharm. Weekblad*, 1939, 76, 1257–1258.)—A patient who had been undergoing treatment with sanocrysin developed indications of poisoning (*e.g.* diarrhoea) after twelve 100-mg. injections, these being equivalent to 436 mg. of gold. It was desired to ascertain if gold was present in the faeces, and 66 g. of these were therefore dried (weight, 7 g.), and ignited (ash, 900 mg.). The ash was extracted repeatedly with dilute hydrochloric acid, the residue being heated again after each extraction; the final residue consisted principally of black powder containing particles of sand. This was extracted with *aqua regia*, the solution was evaporated, and the residue (weight, 5 mg.) was dissolved in water. This solution was yellow, had a metallic taste and, when evaporated in a porcelain crucible, left a blue-black deposit on the walls. The concentrated liquid gave the characteristic crystals of thallium chloroaurate with thallium nitrate solution, and in this way 1 mg. of gold was detected in the 66 g. of faeces. J. G.

Isolation and Properties of Crystalline Papain. A. K. Balls and H. Lineweaver. (*J. Biol. Chem.*, 1939, **130**, 669–686.)—Crystalline papain was prepared from papaya latex by precipitation successively with different amounts of ammonium sulphate and sodium chloride at suitable *p*H values in presence of sodium cyanide. The presence of the cyanide or of some similar activator, such as sulphide or cysteine, was essential for the preparation of crystals of high activity. It was significant that the highest activity obtained appeared to represent a maximum value per unit of protein nitrogen, which was the same for preparations made in several different ways. The crystalline enzyme was found to digest haemoglobin with a velocity comparable with that of pancreatic proteinases, and to bring about clotting of milk and hydrolysis of hippurylamide. Crystalline papain was usually obtained in the form of thin needles, the crystal form apparently being the same whether the material possessed high or low activity. These needles changed on standing in contact with water for several months into large plates having elongated hexagonal faces. The isolated protein was but slightly soluble in dilute salt solutions, particularly at low temperatures, and was soluble in 70 per cent. alcohol. Its isoelectric point was about *p*H 9. Osmotic pressure measurements, observation of the sedimentation in the ultra-centrifuge and the behaviour with iodoacetic acid, all pointed to a value of about 30,000 for the molecular weight of papain. Analysis indicated the presence of 15·5 per cent. of nitrogen, 1·2 per cent. of total sulphur and 1·0 per cent. of cysteine sulphur, but no phosphorus. Amino-nitrogen estimations suggested the presence of 8 amino groups per molecule, whether the material was active, reversibly inactive or irreversibly inactive. Considerable doubt was thrown on the validity of porphyrindin and nitroprusside as indicators of sulphydryl groups in proteins, because they gave negative results with papain, whilst other reagents indicate the presence of such groups. F. A. R.

Ultra-violet Absorption Spectrum of Papain. J. S. Fruton and G. I. Lavin. (*J. Biol. Chem.*, **1939**, **130**, 375–381.)—The absorption spectrum of a 0·5 per cent. solution (*p*H 4·5) of purified papain was obtained with the aid of a Spekker spectrophotometer and a small Hilger quartz spectrograph. The curve showed a maximum at about 280 *mμ* and a minimum at 250 *mμ*. A solution of papain in *N* hydrochloric acid showed a similar curve. The absorption spectrum was also obtained by the use of the continuous light source of a hydrogen discharge tube in conjunction with a quartz Baly cell. This revealed the presence of a narrow band at 290 *mμ*, attributed to tryptophane. The selective absorption due to tyrosine and phenylalanine, however, could not be observed, although tyrosine was actually isolated from the hydrolysed papain and identified. The absorption spectrum of the enzyme after hydrolysis with boiling 20 per cent. hydrochloric acid was different from that of the unhydrolysed material. As might be expected, the tryptophane absorption had disappeared, and the solution now showed strong band absorption at 274 and 282 *mμ*, corresponding closely with the absorption bands of tyrosine. Thus the absence of the absorption bands of tyrosine from the spectrum of a protein solution cannot be interpreted as establishing the absence of tyrosine in the protein. No satisfactory explanation can yet be offered for the non-appearance of the tyrosine bands; for the bands are not masked by the broad absorption of tryptophane in mixtures of the two amino acids, and the absorption curves of several peptides containing one tyrosine residue were found to be similar in appearance to that of tyrosine itself. F. A. R.

Enzymatic Reduction of Cytochrome C; a New Enzyme. E. Haas, B. L. Horecker and T. R. Hogness. (*J. Biol. Chem.*, **1939**, **130**, 425–426.)—A new enzyme, previously noted as a contaminant of a yellow enzyme preparation, has been extracted from yeast, and concentrated 300-fold by fractional precipitation with ammonium sulphate, dialysis, fractional precipitation with alcohol, and repeated adsorptions on aluminium hydroxide with ammonium sulphate elution. The enzyme catalyses the reaction,

cytochrome C + dihydrotriphosphopyridine nucleotide
→ reduced cytochrome C + triphosphopyridine nucleotide.

The protein is water-soluble and colourless, and can be dialysed for 24 hours or dried by desiccation at 0° C. without loss of activity. On being heated to 45° C. for 5 minutes, it loses 80 per cent. of its activity. F. A. R.

Soluble Cytochrome C Oxidase. A. M. Altschul, R. Abrams and T. R. Hogness. (*J. Biol. Chem.*, **1939**, **130**, 427–428.)—Cytochrome oxidase is reputed to be an insoluble enzyme, but a soluble form has been obtained from both brewers' and bakers' yeasts. This can be precipitated from solution by either ammonium sulphate or alcohol, and the precipitate can be re-dissolved in distilled water or buffer solution with retention of its activity. The yeast extract containing the oxidase has been subjected to a centrifugal force equivalent to 35,000 times gravity for 1 hour, and the supernatant solution retained all the activity. The enzyme is inactivated by being heated to 55° C. for 10 minutes, but can be dialysed for 48 hours without loss of activity. The test for the oxidase consists in measuring spectrophotometrically the rate of oxidation of reduced cytochrome C by dissolved oxygen in presence of the enzyme preparation. The oxidation was due to an enzyme and not to metal ions, since the reaction was not catalysed by $Fe^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ or $Mn^{\cdot\cdot}$ ions either in the free state, or in the presence of yeast proteins. The oxidation was inhibited by potassium cyanide, by very small concentrations (1γ per ml.) of catalase, and in the dark by carbon monoxide. F. A. R.

Effect of Orange Juice on Calcium Assimilation. C. S. Lanford. (*J. Biol. Chem.*, **1939**, **130**, 87–95.)—To test the suggestion made by earlier workers, that orange juice favours the retention of calcium in children, a group of young rats was given a small supplement (5 ml. daily) of orange juice in addition to a basal diet of wheat and milk, whilst another group, as similar as possible, was given the basal diet only. At the end of the experimental period, each group was killed and the calcium-content of the carcases was determined. By subtracting from each value thus obtained the average calcium-content of male or female rats of the same age as the animals at the beginning of the experiment, a figure was obtained for the amount of calcium retained by each individual during the experiment. At the same time, by analysing the food, a figure was obtained for the calcium consumed by each individual. From these two figures the percentage retention of calcium by each animal was calculated. It was found that the proportion of calcium thus stored in the body was 8 per cent. greater in the group that received the orange juice than in the control group. The improved assimilation was noted in every instance, and is believed to be statistically significant. Moreover, the total (as well as the percentage) storage of calcium was higher in the former group, notwithstanding a somewhat lower intake than that of the control animals. It was also noticed that the animals given orange juice grew, on the average, about 10 per cent. more rapidly than did the controls. F. A. R.

Sterols of Alfalfa Seed Oil. L. C. King and C. D. Ball. (*J. Amer. Chem. Soc.*, **1939**, **61**, 2910–2912.)—About 4 per cent. of the oil extracted from alfalfa seed with ethyl ether is unsaponifiable matter, which consists of about 35 per cent. of crystalline substances and 65 per cent. of a clear reddish oily liquid. The oily fraction gives a positive Liebermann–Burchard reaction, but only colours the sulphuric acid layer in the Salkowski reaction. The Whitby B reaction (*Biochem. J.*, **1928**, **17**, 5) is positive. The crystalline material has been found to consist primarily of a sterol very similar to, or identical with, the α-spinasterol of Hart and Heyl (*J. Biol. Chem.*, **1932**, **95**, 311), and to have the formula $C_{29}H_{48}O$.
D. G. H.

Preparation of Sterols from Crude Soya-bean Oil. H. R. Kraybill, M. H. Thornton and K. E. Eldridge. (*Amer. Chem. Soc.*, *Div. Agric. and Food Chem.*, *Meeting*, Sept., **1939**, *Absts.*, 4–5.)—Crude soya-bean oil was treated with an adsorbent, which removed the phosphatides, the sterol glycoside and a part of the sterols. Extraction of the adsorbate with acetone gave an oil containing all the adsorbed sterols and a part of the glycoside, but none of the phosphatides. The glycoside was insoluble in the oil and was filtered off. This procedure effected a four-fold concentration of the sterols, and the process was carried still further by continuous extraction with methyl alcohol, the final concentrate containing

3 to 5 per cent. of sterols. A considerable part of the sterols crystallised out in a state of purity, and the remainder was isolated by saponification of the residue. Thus 325 kg. of adsorbed oil yielded 234 g. of sterol glycoside, 768 g. of purified sterol by crystallisation, and 1010 g. after saponification. Stigmasterol was isolated from the sterols by the usual method. F. A. R.

Sterol Glucoside from Expressed Soya-bean Oil. M. H. Thornton, H. R. Kraybill and J. H. Mitchell, Jr. (*Amer. Chem. Soc., Div. Agric. and Food Chem., Meeting*, Sept., 1939, *Absts.*, 4.)—By treating crude soya-bean oil with an adsorbent and extraction of the adsorbate, a sterol glucoside, m.p. 267° to 270° C. (with decomp.), was obtained. It formed a tetra-acetate, m.p. 165° to 166° C. $[\alpha]_D^{20} = -24{\cdot}5°$. The glucoside was hydrolysed to *d*-glucose and a mixture of sterols (m.p. 133° to 134° C. $[\alpha]_D^{20} = -45{\cdot}94°$), from which stigmasterol was isolated to the extent of 20 per cent. by the usual procedure. F. A. R.

Preparation of Vitamin B_6 from Natural Sources. R. D. Greene. (*J. Biol. Chem.*, 1939, **130**, 513–518.)—The ferric chloride reaction discovered by Keresztesy and Stevens (*J. Amer. Chem. Soc.*, 1938, **60**, 1267) was found to be of value in the estimation of vitamin B_6 in rich concentrates. Standard tubes 1 cm. in diameter, containing 10 to 100γ of crystalline vitamin B_6 (m.p. 207° to 208° C.) in 1 ml. of water were prepared. One drop (0·03 ml.) of a 10 per cent. ferric chloride solution was added to the contents of each tube and to 1 ml. of the unknown solution previously made neutral. The vitamin B_6 content was estimated by comparing the red-brown colour of the unknown solution with those of the standards. F. A. R.

Vitamin C in Blackcurrant Juice. W. H. A. Elliott. (*Brit. Med. J.*, 1939, II, 830–831.)—Attention is directed to the nutritional value of blackcurrant juice, and especially to its high vitamin C content, which is 50 per cent. higher than that of the common citrus fruits. The juice can therefore be used as an excellent substitute for the latter, and if depectinised, is easily tolerated by all. A sample contained 25·4 per cent. of fructose, 26·0 per cent. of glucose and 1·7 per cent. of sucrose, 11 parts of iron per million and 77 mg. of vitamin C per 100 ml. It yielded 0·36 per cent. of ash. The added sugar is inverted in the process of maturing. A daily dose of 1 to 1·5 oz. should contain sufficient vitamin C to maintain good health. F. A. R.

Isolation of Vitamin K_1. S. B. Binkley, D. W. MacCorquodale, S. A. Thayer and E. A. Doisy. (*J. Biol. Chem.*, 1939, **130**, 219–234.)—Crude petroleum spirit extracts of alfalfa were subjected to a modified chromatographic adsorption, different adsorbents being used. First, one or two adsorptions on Decalso (an artificial zeolite) were carried out, which effected about 20- to 40-fold concentration. Two subsequent adsorptions on Permutit gave a 5- to 10-fold and a 2- to 5-fold concentration, respectively. Finally, adsorption on Darco (a type of activated charcoal), after removal of some inert material by crystallisation from absolute ethyl alcohol, gave fractions consisting of the substantially pure vitamin. In all the above adsorptions the columns were fractionally eluted by means of petroleum spirit containing gradually increasing amounts of benzene. Vitamin K_1

thus prepared was a pale yellow oil, melting at about −20° C. Its analysis agreed with the formula $C_{31}H_{46}O_2$, and on hydrogenation it absorbed 8 atoms of hydrogen. The ultra-violet absorption curves showed maxima at 243, 248, 261, 270 and 323*mμ*, with an extinction coefficient of $E^{1\%}_{1\,\mathrm{cm.}} = 540$ at 248*mμ*. When heated under reflux with acetic anhydride and zinc and a little fused sodium acetate the vitamin was converted into the diacetate of dihydro-vitamin K_1, which formed characteristic needles (m.p. 62° to 63° C.) after several recrystallisations from petroleum spirit, methyl alcohol and ethyl alcohol. This substance had one-half the biological activity of vitamin K_1, and on treatment with methyl magnesium iodide it was converted back into the vitamin, with restoration of the original activity.

F. A. R.

Derivative of Vitamin K_1. H. J. Almquist and A. A. Klose. (*J. Biol. Chem.*, 1939, **130**, 791–793.)—A vitamin K_1 concentrate was subjected to prolonged hydrolysis with dilute hydrochloric acid in acetone. On the addition of hexane and water there appeared a purple pigment which was preferentially soluble in the aqueous acetone layer. The vitamin appeared to be unaffected by this treatment, and passed quantitatively into the hexane layer. This was washed with alkali and water, dried and evaporated, and the residual oil was hydrolysed with dilute sodium methoxide solution. An intense purple colour was produced, which gradually changed to a permanent reddish-brown colour. The alkaline solution was washed repeatedly with hexane, and then slightly acidified (which changed the colour to yellow) and extracted with hexane. The extract was repeatedly washed with alkali and water, and the pigment partitioned several times between hexane and methyl alcohol by altering the *p*H of the solution. Finally, the product was freed from hexane and distilled in a molecular still. Analysis agreed with the formula $C_{31}H_{50}O_4$, and a determination of the molecular weight (Rast) indicated a value of 500, which confirms the suggested composition. Since vitamin K_1 has the formula $C_{31}H_{46}O_2$, the action of sodium methoxide would thus appear to result in the addition of 2 atoms of oxygen and several atoms of hydrogen. F. A. R.

Growth Factors in relation to Plant Growth. J. Bonner. (*Amer. Chem. Soc., Div. Agric. Food Chem., Meeting,* Sept., 1939, *Absts.*, 13–14.)—It is possible to cultivate *in vitro* root tips that have been isolated from the plant and induce them to grow into mature roots provided that they are supplied with an appropriate nutrient solution. This must include, besides inorganic salts and a carbohydrate, other factors that vary with different plants. Thus vitamin B_1 is essential to the growth of all species of roots, whilst the pea and radish require nicotinic acid in addition; the tomato requires vitamin B_1, nicotinic acid and vitamin B_6, whilst cosmos roots require vitamin B_2 (lactoflavin?) in addition to these three substances. Some species do not supply their roots with as much vitamin B_1 as their root systems are capable of utilising, and they thus grow more luxuriantly if they are watered with a vitamin B_1 solution. In addition, vitamin B_1 has been found in certain instances to promote root growth on cuttings and assist in the restoration of roots after transplanting. It has recently been found that adenine is a growth substance with properties quite different from the foregoing. It affects the growth of leaf mesophyll, and watering plants with a dilute solution of adenine causes an increase in the leaf area. A third group of growth substances is concerned with the initiation of cell proliferation at cut surfaces, whereby rapid healing of wounds in plants is brought about. One of the most active of these substances has been isolated and identified as 1-decene-1 : 10-dicarboxylic acid, or "traumatic acid." It can be regarded as a true wound-healing hormone.

F. A. R.

Physiologically Active Growth Substances and the Responses of Plants. P. W. Zimmerman. (*Amer. Chem. Soc., Div. Agric. Food Chem. Meeting*, Sept., 1939, *Absts.*, 10–11.)—All chemical compounds that have the capacity to induce leaf epinasty (downward bending) of green plants are considered to be physiologically active substances. Some of the more effective of these when used in low concentrations are: ethylene, acetylene, propylene and carbon monoxide; α-naphthalene-acetic acid, α-naphthalene-glyoxalic acid, α-naphthalene-glycollic acid, and α-naphthyl-acetonitrile; β-naphthoxy-acetic acid, β-naphthoxy-acetamide, β-naphthoxy-propionic acid, β-naphthoxy-*n*-butyric acid and β-naphthylglycine; β-indole-acetic acid, β-indole-propionic acid, and β-indole-butyric acid; phenylacetic acid, cinnamic acid, *m*-nitro cinnamic acid, N-phenylglycine ethyl ester and fluorene-acetic acid. The salts and esters of the acids are also effective. Growth substances may be applied to plants in solution or in the form of vapour. Responses involving cell elongation can be observed within half-an-hour; swelling of the tissue occurs within 5 to 10 hours, and the induction of roots requires 3 to 10 days. Besides epinasty of the leaves, growth substances may produce negative and positive local curvatures of stems, abnormal geotropic curvatures of stems and leaves, change in rate of metabolism, swelling of treated tissues, adventitious roots on stems, leaves, roots and floral parts, retardation in rate of elongation of roots, seedless development of fruit, and "desensitisation" of the sensitive plant (*Mimosa*).

F. A. R.

Development of Seedless Fruits (Parthenocarpy) by Use of Synthetic Growth Substances. F. G. Gustafson. (*Amer. Chem. Soc., Div. Agric. Food Chem., Meeting*, Sept., 1939, *Absts.*, 11–12.)—In nature, seedless fruits, such as bananas, oranges, grapes and cucumbers, are sometimes produced without fertilisation, and consequently without the development of embryos and seeds. Parthenocarpy has been artificially induced with the help of certain chemicals. Thus, treatment of the pistils in the flower-bud stage of the tomato, petunia and salpiglossis with synthetic growth substances such as phenylacetic acid, indole-propionic acid and indole-acetic acid, led to the formation of seedless but otherwise normal fruits. In the first experiments the chemicals were mixed with lanolin, and the paste (0·5 to 5 per cent. hormone) was applied to the pistil after removal of the stamens. An alternative method of administration is to spray the female flowers with dilute (*e.g.* 0·0001 per cent.) solutions, whilst results have even been obtained by simply watering the plants with solutions of the hormones. The most successful substances are indole-butyric acid and α-naphthalene acetic acid. The method is at present much too expensive for commercial use, but the discovery of less time-consuming methods of applying the hormones might make the process a practicable one.

F. A. R.

Bacteriological

New Method for the Conservation of Milk. J. G. Davis. (*Nature*, 1939, 143, 1025; *Bull. Hygiene*, 1939, 14, 708.)—By adjusting the *p*H to 5·2 and maintaining milk at a temperature of 36° to 38° C. it can be kept fresh for about 2 weeks. The number of bacteria present decreases in the first week, but after two weeks it increases and they become innumerable. The following results are typical of series of counts obtained with milk adjusted to *p*H 5·15:

Age in days	0	2	7	21
Colony count per ml.	2,560	460	240	innumerable

The adjustment of the *p*H to 5·2 is effected by adding 4 ml. of *N* hydrochloric acid to 100 ml. of the milk. The acid is quickly stirred in so as to avoid local precipitation of casein, and before use the milk is neutralised with *N* sodium hydroxide. A slightly salty taste results—too slight, however, to be detected by casual tasting. By holding anaerobically at lower temperatures and adjusting to lower *p*H values milk can be kept for even longer periods.

[Anaerobes, however, commonly produce such disagreeable odours and taste that anaerobic conservation is hardly to be recommended.—ABSTRACTOR.] D. R. W.

Skunk-like Odour of Bacterial Origin, in Butter. T. J. Claydon and B. W. Hammer. (*J. Bact.*, 1939, 37, 251–8; *Bull. Hygiene*, 1939, 14, 637.)—A skunk-like odour was found to have developed in three samples of unsalted butter (from the same factory) which had been stored at 21° C. for 2, 3 and 4 days; when the tainted butter was inoculated into fresh pasteurised cream and the cream churned, the same defect was reproduced. Attempts to isolate the organism responsible for the production of this odour were unsuccessful when using beef infusion agar, but by using casein agar a bacterium was isolated which gave the same skunk-like odour in litmus milk in 1–2 days, and when inoculated into cream caused the same odour to develop in unsalted butter made therefrom. Salt apparently has an inhibitory effect upon the growth of this organism, for the odour does not appear in salted butter. The characteristics of the bacterium are described in detail: it is non-sporing, actively motile and easily killed by heat; its optimum temperature is 21° C., and it has few biochemical characters. D. R. W.

Thermal Death Time of Micro-organisms encountered in the Brewing Industry. S. S. Epstein and F. D. Snell. (*Amer. Chem. Soc., Div. Agric. and Food Chem., Meeting*, Sept., 1939, *Absts.*, 9.)—The thermal death times of 21 cultures of organisms commonly encountered in the brewing industry were estimated. These included the following pure cultures: 5 *Sarcina* (*Pediococcus*) strains, 2 *Lactobacillus* strains, 2 *Acetobacter* strains and 8 yeasts. The other cultures used comprised a strain of *Lactobacillus* taken directly from a very turbid pasteurised light bottled beer, and mixed cultures obtained from an infected storage ale, an infected storage beer and a spoiled draught beer. All the bacteria and yeasts were killed by exposure to 60° C. for 10 minutes, and the spores at 58° C. in 20 minutes or at 60° C. in 15 minutes. Thus the standard practice of pasteurisation at 60° C. for 20 minutes should render beer and ale free from all living micro-organisms commonly encountered. F. A. R.

Infection of Beer with *Acetobacter capsulatum* Shimwell and *Achromobacter anaerobium* Shimwell. A. A. D. Comrie. (*J. Inst. Brewing*, 1939, 45, 342–4.)—Two types of beer disease due to bacteria similar to those named above were described by Shimwell in 1936 and 1937, the first giving ropiness to the beer and the second giving the beer a peculiar odour and flavour. The descriptions of these bacteria and their biological characters are given in detail; briefly they are as follows:

Acetobacter capsulatum.—Rods about 0·5 × 2μ long with some coccoid forms; motile in young cultures; non-sporulating; Gram-negative; capsules demonstrated by iodine but not by Muir and Gin's stain; good surface-growth on beer agar; rapid growth with haze in hopped beer-wort with slight ropiness; aerobic, non-facultative; optimum temperature 30° C.; *p*H range 3·3 to 4·7; tolerates 6 per cent. of alcohol; glucose, maltose and sucrose slowly attacked, and lactose very slowly, with production of acid but no gas; alcohol converted into acetic acid.

Achromobacter anaerobium.—Rods usually 1 × 2μ; occasionally 4 to 6μ long; very motile; non-sporulating; Gram-negative; grows with difficulty on agar, better on gelatin. In liquid media (anaerobically) no growth in sugar-free beer or yeast extract; intense haze and gas production (entirely CO_2) with invert sugar or glucose present; no growth with maltose or sucrose; anaerobic, non-facultative; a trace of carbon dioxide is necessary for growth; optimum temperature 20° C.; thermal death-point 57° C.; *p*H range 3·7 to 4·7. The organism will develop in sealed bottled beer; fermentation very vigorous, with opalescent haze production.

D. R. W.

Bacterial Flora of Flies caught in Food Stores in the City of Manila. G. C. de la Paz. (*Monthly Bull., Bureau of Health, Manila*, 1938, **18**, 393–412; *Bull. Hygiene*, 1939, **14**, 635.)—Forty-three food stores and other premises were investigated in the period May to October, 1937, and in these flies were caught, the great majority being of the genus *Musca*. These were examined bacteriologically; first they were washed externally and the washings were examined, and then, after they had been sterilised externally, the inside portions were examined. The bacteria found were classified into 10 groups. The *coli-aerogenes* group was found in every sampling, the *Proteus* group in 21 per cent. externally and 34 per cent. internally, the *Salmonella* group in 37 per cent. externally and 43 per cent. internally, the *Eberthella* group (including *B. typhosum*) in 23 and 24 per cent., respectively, the *Shigella* group (the dysentery bacilli) in 46 and 60 per cent., *Staphylococci* in 21 and 14 per cent., *Streptococci* in 5 and 8 per cent., and *Pseudomonas* in 5 and 3 per cent., respectively. The author considers that these results show that flies constitute a very serious menace to public health in Manila. D. R. W.

Toxicological

Contamination of Foodstuffs with Volatile Toxic Substances. F. Schoofs. (*J. Pharm. Belg.*, 1939, 21, 793–802.)—This subject has attained great importance recently owing to the practice of fumigating ships and warehouses and the use of toxic gases in warfare. Dichlorodiethyl sulphide (mustard gas, Ypérite, Yellow Cross, Lost) is difficult to remove from food material owing to its high boiling-point (216° to 219° C.), its solubility in fats, and its property of being easily dispersed into fine droplets. Packing in hermetically sealed glass, porcelain or metal vessels, or in sufficiently thick cellophane is the only method of protection that can be generally recommended. Paper affords only moderate protection. According to Bruère (*Bulletin des Docteurs en Pharmacie de France*, Paris, 1933), the following methods of decontamination are applicable to certain foodstuffs. Unpacked foods protected by a natural non-porous cuticle (*e.g.* green vegetables, fruit, potatoes) may be steeped rapidly in a hypochlorite solution and subsequently washed in sodium carbonate solution containing 5 per cent. of sodium thiosulphate. With cereals, haricot beans, lentils, etc., which swell easily, this treatment should not be prolonged. Porous substances, such as bread or biscuits, may be re-cooked in an oven. Small stocks of flour should be destroyed, but chlorination may prove applicable to large stocks. Butter, margarine, lard, chocolate, etc., absorb mustard gas very easily, especially when it contains carbon tetrachloride, and no method of decontamination is applicable to these foods.

Phosgene (Collongite) is easily absorbed by moist foodstuffs, which are rendered unfit for use by the hydrochloric acid produced by its decomposition. Dry foods may be renovated by vigorous ventilation in a current of dry, warm air. Bread and minced meat were exposed to an atmosphere containing phosgene for 18 hours and afterwards to pure air for 2 hours. The foods were then extracted with alcohol, and the extracts were titrated with alkali (phenolphthalein as indicator), with the following results (ml. $N/10$ per 10 g.):—bread before exposure 0·9, after exposure 46·5; meat before exposure 4·1, after exposure 9·2 (outer surface) and 7·1 (interior). A sample of pure water treated in the same manner was found to contain 0·9204 g. of chlorine ion per litre. Chloropicrin (Aquinite, Vomiting Gas) is sometimes mixed with preparations of hydrocyanic acid used as fumigants. According to the method of Sytschew (Plucker, *Z. Unters. Lebensm.*, **1934**, **68**, **313**; Abst., ANALYST, 1934, **59**, 841) it may be detected by treating the suspected material with a current of air which is then bubbled through a solution of potassium iodide in methyl alcohol. Potassium chloride and nitrite are formed and may be determined. Deckert and Prathithavanija (*J. Pharm. Belg.*, 1939, **21**, 129) have described a colorimetric method whereby small amounts of chloropicrin in foods are detected by treatment of the benzene extract with dimethylaniline in presence of oxygen. Moist foods contaminated with chloropicrin are rendered unfit for use, as the fatty portions retain it tenaciously. Dry foods may be treated with a strong current of air.

Chlorovinyldichloroarsine (Lewisite) is difficult to remove from contaminated food. Diphenylchloroarsine (Clark I) and diphenylcyanoarsine (Clark II) and similar arsenical compounds can be detected by submitting the food to a strong current of air which is then passed through a cotton-wool plug. An alcoholic extract of the plug may be titrated with a solution of iodine in benzene (Sieverts, *Z. angew. Chem.*, 1922, **35**, 17). Filter-paper has been suggested as a means of protecting food from the persistent arsines. Hydrocyanic acid gas (Forestite, Manganite) will probably not find extensive use in warfare, but it is widely used as a fumigant. Fruit and fresh legumes absorb it only feebly (Buttenberg and

Weiss, *Z. Unters. Lebensm.*, 1924, **48**, 104; Abst., ANALYST, 1924, **49**, 533), but it is more easily absorbed by moist sweet fruits (dates, raisins, etc.), although its concentration in these rarely exceeds 3 mg. per 100 g. Meat was found to absorb 0·92 mg. per 100 g., and the concentration fell to about one-half after aeration. Rye and wheat flours absorbed 0·43 and 0·86 mg. per 100 g. respectively, all of which was removed by aeration. Experiments showed that meat retained some of the gas in combination and not recoverable by direct distillation with tartaric acid. Experiments with milk showed that it may retain 41 mg. per litre, which, in view of its use for infant feeding, must be regarded as a dangerous amount. Oils and fats absorb little, but the water present in butter and margarine favours its fixation. For protection, food should be packed in sealed containers. Paper may afford protection but, when moist, it interferes with aeration, which is often the most effective means of treatment. The Paris municipal authorities have suggested that in the event of contamination of the water supplies of the city by gases used in warfare, the public could be warned of the danger by the addition of fluorescein to the water (Bruère, *loc. cit.*). According to Bonham-Carter and Bird (" *Technique Sanitaire et Municipale*," 1939, p. 31) the filters will arrest mustard gas and lewisite, but this does not remove the danger if the service reservoirs are contaminated. Thomann (*J. Pharm. Belg.*, 1938, **20**, 840) has shown that mustard gas is slightly soluble in water, but undergoes hydrolysis with formation of dithioglycol, a reaction that is accelerated by heat. If water is to be boiled, however, it will be necessary to prevent contamination of the atmosphere at the place of operation. Other means of purification that have been suggested are treatment with hypochlorite, bleaching powder, potassium or calcium permanganate, sodium hyposulphite or active carbon. A. O. J.

Physio-toxicology of the War Gases. L. Herlant. (*J. Pharm. Belg.*, 1939, **21**, 820–822.)—War gas was originally defined as "any substance which at a concentration of 4 g. per cubic metre in air creates an atmosphere capable of provoking fatal lesions in the respiratory apparatus of a man or animal that remains in it for 5 minutes." The number 4 is a limiting value; later, substances were used which were active at much lower concentrations—*e.g.* phosgene (0·500 g./cm., fatal in 1 minute). With some arsines even at 0·0005 g./cm. the atmosphere cannot be tolerated; tear gases have been used at 0·300 g./cm. Toxicological activity is not the only condition necessary for military use; from this point of view carbon monoxide, arsine and hydrogen cyanide are comparatively unimportant, whilst a large number of liquids, even with high b.p., and of solids dispersed in air (aerosols) must be included among the "war gases." The gases have been classified as (1) *Suffocating*: act on the lungs and are generally fatal at low concentration and after not very prolonged exposure: *e.g.* chlorine, phosgene, diphosgene, chloropicrin, etc. (2) *Irritants*: (*a*) Sternutatory; cause coughing and vomiting (through saliva in stomach); high concentration causes physical debility: *e.g.* various arsines. (*b*) Lachrymatory: produce tears and prevent vision for ¼ to 1 hour; in the concentrations used they seldom have other effects: *e.g.* benzyl bromide, halogenated ketones. (*c*) Labyrinthic: disturb mobility and cause falling: *e.g.* dichloromethyl ether. (3) *Vesicants*: burn unprotected skin and mucous membranes; when breathed are in class (1): Lewisite and Yperite (4) *Haemoglobin poisons*, and (5) *General poisons*. These produce death by stopping vital processes or nervous centres, by action either on the haemoglobin or on the nervous system. In spite of their high toxicity, extreme volatility and low vapour density, they have been little used. Carbon monoxide, nitrous vapours and hydrogen cyanide are examples of classes (4) and (5). The Index of Toxicity of a gas, as defined by Haber, is the product of the quantity of gas in milligrams per cubic metre of air and the time in minutes that will cause the death of a subject, weighing 1 kg., which breathes the atmosphere. Thus, $I = q \times t$.

For phosgene, $I = 450$. If a man weighing 70 kg. breathes 8 litres of air per minute, the weight causing death in one minute is

$$8 \times \left(\frac{450}{1000}\right) \times 70 = 252 \text{ mg. of phosgene.}$$

As these results have been determined on animals, they must not be considered absolute for human beings; protective and eliminative factors also vary from one individual to another, but the Haber numbers give a relatively accurate measure of toxicity.

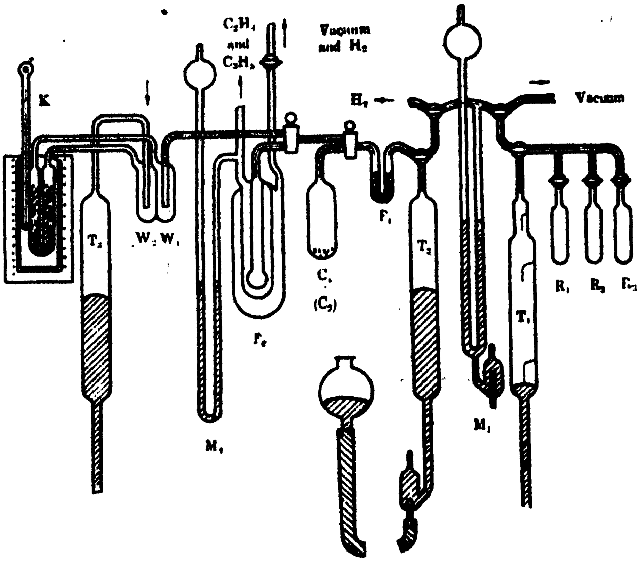
TABLE OF TOXICITY INDICES (HABER)

Substance	War name		Index
	French	German	
Carbon oxychloride	Collongite	—	450
Trichloromethyl chloroformate	Surpalite	Perstoff	500
Dichloroethyl sulphide	Yperite	Lost	1,500
Chloropicrin	Aquinite	Klopp	2,000
Ethyl chlorosulphate	Sulvinite	—	2,000
Ethyl bromoacetate	—	Bn-Stoff	3,000
Chloroacetone	—	—	3,000
Acrolein	Papite	—	3,000
Bromoacetone	Martonite	B-Stoff D	4,000
Xylyl bromide	—	T-Stoff D	6,000
Chlorine	Berthollite	—	7,000
Hydrocyanic acid	Forestite	—	1,000 to 4,000(?)
Carbon monoxide	—	—	70,000(?)

E. B. D.

Gas Analysis

Dry Method for the Analysis and Separation of Components of Hydrocarbon Gas Mixtures. K. Morikawa. (*J. Soc. Chem. Ind., Japan*, 1939, 42, 129–133B.)—The author has developed a "dry" method for small quantities of gases which is claimed to be more precise than the existing "wet" methods based on absorption in solutions of reagents. The apparatus used is shown in the figure. A suitable quantity of the gas to be analysed is taken out of one of the tubes R by means of the burettes T_1 and T_2, and its volume is measured at constant volume by the pressure exerted in the U-tube manometer M_1. The burettes are calibrated at each of the internal glass points shown; each has a capacity of about 250-ml. and serves the purpose of burette, Toepler pump, and gas-circulating pump. They may be surrounded with air-jackets to protect them from temperature fluctuations. F_1 is a small trap filled with small copper granules and is cooled to $-50°$ C. or $-80°$ C., depending on the nature of the gas under examination, so as to remove mercury vapour and possible water, both of which are serious poisons for copper and nickel catalysts. When not in use the catalysts are kept in an atmosphere of hydrogen. C_1 is the copper catalyst tube of about 70-ml. capacity, containing 1 to 1·5 g. of active copper catalyst. A second catalyst tube, C_2 (not illustrated), of about 100-ml. capacity and containing 1 to 2 g. of an active nickel catalyst supported on kieselguhr, is connected at the same point as C_1, but has its own three-way stopcock. F_2 is the fractionating vessel. K is the copper and copper oxide catalyst tube containing 5 to 10 g. of partly reduced copper oxide granules, the particles being about 1 mm. diameter; this catalyst is protected from mercury vapour by the two traps W_1 and W_2, each having a volume of about 10 ml.



Methods of Analysis.—(1) *Hydrogen by means of Copper Oxide.*—The hydrocarbon and hydrogen mixture of known volume is circulated backwards and forwards through the copper and copper oxide tube K, by means of the burettes T_2 and T_3, and the water formed by oxidation is frozen out in W_1 and W_2. After the hydrogen has been completely removed the volume is determined again by pumping all the gas into the burette T_1 by means of the Toepler pump T_2, the volume change giving the hydrogen-content. The error in test determinations was less than 0·5 per cent. This method may be used with deutero-hydrocarbons in isotopic investigations.

(2) *Olefines by Hydrogenation on Copper.*—A copper catalyst has been found to be as good as a nickel catalyst, and has the additional advantages of a smaller tendency to promote undesirable side-reactions, small adsorptive capacity for the gases under consideration, and no tendency to promote exchanges in the deutero-alkyl hydrocarbons at temperatures at which hydrogenation proceeds rapidly.

The working temperature was generally 50° to 60° C., though the copper catalysts promote hydrogenation even at 0° C. The quantity of olefine was determined by the pressure difference before and after hydrogenation and was checked by the hydrogen volume difference before and after hydrogenation. The remaining hydrogen was determined by freezing out all the hydrocarbons (when methane was absent) with liquid air round trap F_1, sufficient time being allowed for the copper granules to cool.

(3) *Saturated Hydrocarbons by Hydrogenating Decomposition on Nickel.*—The vapour pressure of methane at 80° to 82° K. is 20 to 30 mm., so that methane can be extracted from the frozen gas mixture at these temperatures. The gas sample is frozen in F_1, the methane is extracted, and the frozen hydrocarbons are vaporised, and then frozen and extracted again, T_1 serving as the storage bulb for the methane and T_2 as the Toepler pump for extraction. The residual hydrocarbons are analysed by hydrogenating them to methane in presence of a nickel catalyst and an excess of hydrogen at 250° to 300° C. Methane remaining adsorbed on the catalyst by adding hydrogen and evacuating, the hydrogen is oxidised by the copper oxide C_1, and the methane is collected and added to that previously recovered. If carbon dioxide is present in the gas sample, it can be determined by adsorption in an ascarite or soda-lime tube attached at the same point as C; if carbon monoxide is present, it may be burned to carbon dioxide on the copper and copper oxide catalyst at the same time as the hydrogen is determined, and the carbon dioxide produced may be measured. Alternatively, carbon monoxide may be determined directly by means of the reaction $5CO + I_2O_5 = 5CO_2 + I_2$. With samples of 3 to 20 ml. volume the average error in any of these determinations was found to be about 0·5 per cent.

Separation of the Hydrocarbons by Fractionation at Reduced Pressures.—The method developed was intended to be only semi-quantitative, but yields pure fractions from a mixture of aliphatic hydrocarbons, so that their protium-deuterium content can be ascertained by thermal conductivity analysis. The fractionation vessel shown in the figure consisted of three concentric tubes with diameters 8, 19, and 28 mm.; the inner tube was 12 cm. long. The second tube served as the low-temperature bath and was connected with two 2-litre storage flasks, one containing ethylene and the other propane. The outer tube was connected with a high-vacuum system and with a source of hydrogen. The apparatus was thoroughly evacuated, about 20 mm. of hydrogen were introduced into the outer space, and the whole was cooled by immersion in liquid air. About one-half of the ethylene was then condensed in the middle space and its temperature was followed by its vapour pressure as measured on manometer M_2. At a suitable temperature the gas sample was introduced into the inside tube and frozen out. The hydrogen was evacuated thoroughly, the full liquid air bath being kept in place, and finally the remaining half of the ethylene was allowed to condense in portions until the desired bath-temperature was obtained. The rate of rise of temperature of the bath could be controlled by the rate of evaporation of the ethylene and so by the volume of its vapour phase. With an ethylene vapour phase volume of about 550 ml. and under the conditions described a temperature rise of 10° to 20° C. per hour was observed and proved to be satisfactory. The gas was distilled from F_2 into the sample bulbs R, which were cooled in liquid air. The distillation pressure was read on manometer M_1. As the bath temperature rose the gas pressure increased to a maximum, usually 2 to 3 mm., and then fell again to less than 0·5 mm. on passing from fraction C_n to C_{n+1}. The C_2 fraction was separated at bath temperatures up to ~100 mm. of *ethylene* and the C_3 fraction at bath temperatures up to ~100 mm. of *propane*, the propane being substituted for the ethylene as a bath fluid between separations and similar technique being used, except that about half of the liquid air was removed from the Dewar flask surrounding the fractionation column so as to allow a more satisfactory rate of temperature rise. The accuracy of the method is about 5 per cent. The purification of methane in the presence of nitrogen was achieved by using the low temperature trap previously described (*J. Chem. Phys.*, 1937, **5**, 203). In the presence of butane it was found best first to divide the frozen mixture of C_2, C_3 and C_4 into a C_2 plus C_3 and a C_4 fraction, and then to separate the C_2 plus C_3 fraction into its C_2 and C_3 parts. The relatively high solubility of butane in the Apiezon stopcock grease results in appreciable errors in the measurement of the unsaturated hydrocarbons if these measurements are carried out on the hydrocarbon itself, so that it is recommended to use as a criterion the change in hydrogen pressure. E. M. P.

Organic

Identification of Propionic Acid in Presence of Acetic and Butyric Acids. L. Musicant and F. J. Kaszuba. (*J. Amer. Chem. Soc.*, 1939, **61**, 2974–2976.)—A rapid and accurate method of identifying propionates in presence of interfering acetate and butyrate ions is by the use of mercurous nitrate. The crystals of mercurous propionate are well defined and differ to a pronounced extent from those of either mercurous acetate or butyrate, and they are formed readily even when the latter substances are also present. A neutral hydrolysate or test solution is distilled *in vacuo* to dryness, the residue is acidified with conc. phosphoric acid, and the liberated acids are distilled off *in vacuo*. The distillate is collected in a test-tube surrounded by a freezing mixture. A capillary is used to transfer several drops of the acid distillate to a slide, a drop of 5 per cent. sodium carbonate solution is added (the mixture should still react acid to litmus), and the whole is evaporated to dryness. The residue is dissolved in 2 to 4 drops of water, a drop of a saturated solution of mercurous nitrate (acidified with nitric acid to prevent decomposition) is placed alongside and allowed to flow into the test solution, and the precipitate is at once examined under the microscope. Illustrations are given of the crystals of the various mercurous salts: the acetate, propionate, butyrate, acetate-propionate, acetate-butyrate, propionate-butyrate and the acetate-propionate-butyrate. Formates tend to interfere with the analysis when the concentration is equal to, or greater than, that of either of the other anions. If the test substance contains only the sodium salts of the acids mentioned, distillation is not required. D. G. H.

New Method for the Determination of Glycerol in Soaps containing Fillers. W. Schulze. (*Fette u. Seifen*, 1939, **46**, 66–69.)—The usual methods for the determination of glycerol (the dichromate, acetin and Shukoff–Schestakoff distillation methods) are not always satisfactory in presence of filling materials. In particular, the dichromate method, which is satisfactory apart from this, may fail if the filler is organic in nature, and methods of separating the glycerol before the actual determination is made are therefore considered. Attempts to remove the filler by precipitation (*e.g.* with lead acetate, silver carbonate, aluminium sulphate or aluminium acetate) were unsuccessful, owing to the incomplete removal of certain fillers such as tylose. Partial separation of the glycerol by dialysis at room temperature is therefore preferred. The apparatus is a glass cylinder, the base of which consists of a semi-permeable membrane ("Kuprofan"), supported inside a larger glass cylinder; both cylinders are provided with stirrers, which are driven by a common motor. In the inner cylinder is placed a 25 per cent. solution of the sample, and in the outer vessel a 20 per cent. solution of a "synthetic" soap, which is prepared in the laboratory from oleic acid and potassium hydroxide, and which in this instance had a fat-content of 33·3 per cent., but contained no glycerol. After 48 hours the glycerol-content of the liquid in the outer vessel is determined by the dichromate method, and the volumes of liquid in the two vessels are measured. Since equilibrium has been reached the concentrations of glycerol are the same in both vessels, and the glycerol-content of the soap may be calculated. Preliminary experiments, in which water was used in the outer vessel (so that the refractive index could be used to follow the course of dialysis), showed that after 48 hours equilibrium is reached even in presence of soap and/or tylose; although tylose may be present in the original soap, none is found in the outer vessel after dialysis. Several examples are cited. Thus, a solution of 30 g. of a household soap (containing tylose) in 120 ml. of water was placed in the inner vessel and a 20 per cent. solution of the "synthetic" soap in the outer vessel. After 48 hours the glycerol-content of the solution in the latter was determined by the dichromate method, and from a knowledge of this and the volume of liquid present in each vessel a glycerol-content of 0·44 per cent. for the original soap was obtained; the value obtained by calculation from a knowledge of the history of manufacture of the soap was 0·41 per cent. In another instance 10 per cent. of glycerol and 10 per cent. of tylose solution (1 + 4) were added to a 10 per cent. solution of the synthetic soap; the glycerol-content found was 2·42 g., whereas 2·5 g. were actually added. The method may also be used for curd soaps, so long as the whole apparatus is immersed in a water-bath at a temperature which enables dialysis to proceed. Allowance should be made for the presence of sugars, which have the property of diffusing through the type of membrane used, and attaining an equilibrium concentration. J. G.

Determination of Phenols in Hydrocarbon Solvents. L. A. Wetlaufer, F. J. Van Natta and H. B. Quattlebaum. (*Ind. Eng. Chem., Anal. Ed.*, **1939**, **11**, 438–439.)—A method has been worked out for the colorimetric determination of small amounts of phenolic compounds in petroleum solvents used in paints. It is particularly suitable for the determination of the higher alkyl substituted phenols, which are almost or quite insoluble in water. The solvent is extracted repeatedly with 25-ml. portions of dilute potassium hydroxide solution until the final extract gives a negative test for phenol. The repeated extractions are essential, owing to the low solubility in water of the higher alkyl substituted phenols. (Alkali-insoluble phenols containing 8 or more carbon atoms in the side chain do not usually occur in paint solvents.) Twenty-five ml. of the combined extracts are neutralised with dilute sulphuric acid and made up to 100 ml. with glacial acetic acid to liberate the phenols, which are soluble in the dilute acid thus formed. The solution must contain at least 50 per cent. of acetic acid. Duplicate 50-ml. samples are each acidified with a few drops of conc. sulphuric and nitric acids, and the clear solution obtained is warmed on the steam-bath until the yellow colour formed reaches a maximum. After cooling in ice, making the solution ammoniacal converts the nitroso phenol into the deeper yellow quinonoid salt. This solution is compared colorimetrically with a similarly treated standard solution of a phenol, in a Duboscq or Klett colorimeter or in Nessler tubes. Ordinary phenol is the standard for a greenish-yellow colour and *o*-tertiary butyl phenol, which is more often required, for orange-yellow. The method is rapid and direct. One similar in principle has been used for biological materials (*cf.* Stoughton, *J. Biol. Chem.*, 1936, **115**, 293). E. B. D.

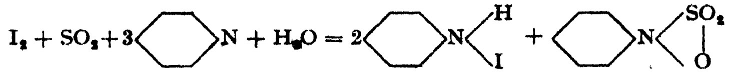
Inorganic

Use of a Solution of Hydrogen Sulphide in Acetone as an Analytical Reagent. M. Péronnet and R. H. Rémy. (*J. Pharm. Chim.*, 1939, **30**, 170–172.)—The authors have endeavoured to overcome the instability of hydrogen sulphide in solution (as used in chemical analysis) by the use of an organic solvent. The gas was prepared from iron sulphide and hydrochloric acid, dried by means of anhydrous calcium chloride, and passed slowly into the following solvents until complete saturation was reached; the corresponding solubilities at 20° C. in g. per litre of solvent are also given (*cf.* Bell, *J. Chem. Soc.*, 1931, 1376):—Hexane, 9·45; benzene, 23·50; toluene, 25·35; chlorobenzene, 20·70; 95 per cent. alcohol, 10·80; acetone, 22·40; dioxan, 12·90; carbon disulphide, 8; thiodiglycol, 7·7; distilled water, 3. The solutions were stored in dry bottles and examined at intervals. The solution in acetone is preferred as a reagent because it has the capacity for dissolving a high proportion of the gas (see above); the resulting solution is miscible in all proportions with water and other organic solvents; after 6 months of normal use, during which time the reagent bottles were frequently opened, it still contained over 10 g. of hydrogen sulphide per litre, the gas-content of the other solutions being then very small. After a year, however, the solution in acetone developed a turbidity on dilution with water, owing to the formation of thio-acetones which are insoluble in water. The solution in dioxan decomposed rapidly, alcohol showed no advantages over water, and thiodiglycol was too viscous to be satisfactory. J. G.

Analytical Procedures Employing the Karl Fischer Reagent for the Determination of Water. I. Nature of the Reagent. D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr. (*J. Amer. Chem. Soc.*, 1939, **61**, 2407–2412.)—In Fischer's method for the determination of water (*Z. angew. Chem.*, 1935, **48**, 394) the wet material is titrated directly with a solution of iodine, sulphur dioxide and pyridine in methanol, the reagent serving as its own indicator. Fischer's outline of the reactions involved does not adequately explain the quantitative results. His reaction

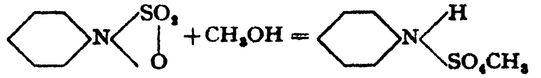
$$2H_2O + I_2 + SO_2.2C_5H_5N + 2C_5H_5N = (C_5H_5N)_2H_2SO_4 + 2C_5H_5NHI \qquad (1)$$

indicates the removal of 2 molecules of water, whereas actually about 1 molecule or less is removed by the unmodified reagent. A study was made of the fundamental molar ratios of the various constituents of the reagent and their relation to water absorption. By working with concentrated solutions, crystalline intermediate products were isolated and identified by optical crystallographic methods and by comparison with synthetic material. The fundamental reaction was found to occur in two stages, *viz.*:



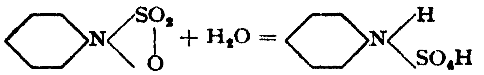
(2)

and



(3a)

Only the first stage involves water absorption, and the amount absorbed is one-half of that required for Fischer's reaction. The intermediate compound (an inner salt of pyridinium hydroxide-N-sulphonic acid) can be isolated, especially if methanol is omitted from the reagent. It was found possible to prepare a modified reagent without methanol, and with this the water absorbed approached the 2 molecules required by reaction (1).



(3b)

The general use of such a reagent is undesirable because the reaction (3) is not specific for water, as is reaction (2), and is not accompanied by a colour change. Also, the water equivalence of this reagent varies greatly with minor differences in technique. By varying the constituents of the reagent individually and determining known amounts of water in dimethylformamide solution, it was found that the minimum ratios of iodine, sulphur dioxide, and pyridine were 1 : 1 : 3. Fischer's equation corresponds with the ratios 1 : 1 : 4 (the unmodified reagent has the ratios 1 : 3 : 10) and is based on the assumption that pyridine forms a normal sulphate. All attempts to prepare this failed, and the acid sulphate was invariably obtained, confirming the smaller ratios found. Although the absence of methanol did not prevent the removal of the brown colour of the reagent by water, an abrupt change in the actual amount of water absorbed occurred as the ratio of methanol to iodine was reduced below 1; above this ratio only minor differences were observed. In the absence of methanol the water absorbed per molecule of iodine at the characteristic end-point varied from 1·1 molecule (when water was added to the reagent) to 1·9 molecules in the reverse process. In presence of 1 molecule or more of methanol, about 0·7 molecule of water was absorbed regardless of the order of mixing. This is evidence that the combination of the reagent with water occurs in two stages, and that methanol can replace water in one stage. The reagent is prepared by dissolving 84·7 g. of iodine in a mixture of 269 ml. of pyridine and 667 ml. of methanol. To this solution, kept cool in ice, 64 g. of liquid sulphur dioxide are cautiously added. The final dark brown solution is about twice as strong as Fischer's reagent, but is essentially the same in other respects. The water-contents of the solvents should not exceed 0·1 per cent., as the presence of 6 per cent. of water will completely exhaust the reagent. The solution deteriorates rapidly during the first week and then more slowly. Little loss of strength occurs if the addition of sulphur dioxide is deferred until a day or two before use. The special form of the reagent for use in presence of ketones is prepared as described above, but 860 ml. of pyridine and 90 ml. of methanol are used instead of the quantities stated. To standardise the reagent 18 ml. of water are accurately weighed and diluted to 1 litre with methanol containing less than 0·1 per cent. of water. Both the solvent and the water solution are titrated with the reagent, and it may be assumed with sufficient precision that the titre of the solution corresponds with the aliquot portion weighed and 98 per cent. of the titre of the amount of solvent present. Substitution of other bases for pyridine was tried and, although quinoline, aniline, dimethylaniline, tri-*n*-butylamine and triethanolamine may be used, pyridine was found to be the most satisfactory. The method is recommended for the determination of water in alcohols, hydrocarbons (including saturated, ethylenic, and aromatic types), carboxylic acids (except formic acid) and esters. Some weak tertiary amines can be titrated directly, but a better and more general method for amines is to dissolve the amine in glacial acetic acid of known water-content. With aldehydes and ketones the unmodified reagent is unsatisfactory, owing to the formation of acetals and ketals, with the large excess of methanol, and consequent liberation of water. By reducing the methanol-content and increasing the pyridine-content as previously described, a reagent that reacts normally in presence of ketones is obtained. Even with this, large amounts of the lower alcohols must not be present. It was believed at first that the active constituents of the reagent were present as a complex compound of pyridine and sulphuryl iodide, but there is no evidence to support this, and the reagent is now believed to be a mixture of the two binary compounds $C_5H_5NI_2$ and $C_5H_5NSO_2$. Fischer's observation that the iodine in the reagent shows practically no tendency to react with ethylenic double bonds has been confirmed. A. O. J.

Thallous Carbonate as an Acidimetric Standard. E. Jensen and B. Nilssen. (*Ind. Eng. Chem., Anal. Ed.*, **1939, 11,** 508.)—The reliability of pure thallous carbonate for the standardisation of *N* hydrochloric acid is confirmed. Thallous carbonate is stable up to at least 150° C.; it does not absorb carbon dioxide and is non-hygroscopic in air having up to 80 per cent. relative humidity. Titration is carried out in the boiling solution; bromocresol purple indicator is preferred. Thallous carbonate can be readily purified by recrystallisation; the use of platinum vessels is advised, as the solution attacks glass slightly. The salt may be tested for impurities by dissolving 0·5 g. in 5 ml. of water; if the solution is perfectly clear, magnesium, calcium, barium, aluminium, iron, manganese and lead are absent; a solution of 0·5 g. in 5 ml. of 2*N* sulphuric acid should give no precipitate or coloration with hydrogen sulphide. Alkali metals may be determined by separating the thallium by precipitation as thallic hydroxide with bromine and ammonia and evaporating the filtrate to dryness in a platinum crucible; after removal of the ammonium salts by heating the residue is weighed; a residue of less than 0·5 mg. from a 5-g. sample of thallous carbonate indicates satisfactory freedom from alkali metal salts. Chloride, nitrate and sulphate may be tested for by the usual methods. S. G. C.

Patent Blue V as a *p*H and Redox Indicator. J. H. Yoe and G. R. Boyd. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1939, **11**, 492–493.)—Patent blue V (the sodium, calcium or magnesium salt of a substituted triphenylmethane sulphonic acid) may be used in aqueous solution (preferably 0·1 per cent.) as an indicator for the colorimetric determination of *p*H over the range 0·8 to 3·0 (colour range: yellow through green to blue); the colour showed good light-stability for 5 days, after which slight fading tended to occur. Solutions of the dye from different sources showed slightly different colours at a given *p*H value. The oxidation potential of various commercial samples ranged from +0·68 to +0·78 volt. The dye may be used as an oxidation-reduction indicator in the titration of iron with ceric sulphate, but chloride must be absent, owing to masking of the colour of the indicator by ferric chloride. S. G. C.

Colorimetric Determination of Iron as Thiocyanate in presence of Hydrogen Peroxide. C. A. Peters, M. M. MacMasters and C. L. French. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1939, **11**, 502–503.)—The addition of hydrogen peroxide is recommended for stabilising the colour in the thiocyanate determination of iron. It is necessary to limit the amount of hydrogen peroxide used, as too much may cause a yellowish interfering colour due to oxidation products of the thiocyanate. To arrive at the correct amount required, it is suggested that a preliminary trial should be made by adding, say, 30 drops of hydrogen peroxide to the iron thiocyanate solution; if a yellowish tinge is produced, a smaller amount, say, 15 drops, should be added to the test-solution. S. G. C.

Colorimetric Method for the Determination of Barium. H. A. Frediani and B. J. Babler. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1939, **11**, 487–489.)—Barium may be determined by precipitation as chromate in the ordinary way from dilute acetic acid and ammonium acetate solution (*vide*, *e.g.* Scott, "*Standard Methods of Chemical Analysis*," 1925), dissolving the precipitate, after filtering off and washing, in 1 : 1 hydrochloric acid, and comparing the colour in a Duboscq colorimeter with that of a solution obtained by carrying out the process on a standard barium solution. Solutions containing chromic acid equivalent to 0·3 to 1·0 mg. of barium per ml. afforded the best range of colours for comparison; at a lower concentration the solution is insufficiently coloured, whilst stronger solutions are difficult to match. The presence of strontium leads to high results, but its effect may be avoided, as in the gravimetric method, by careful double precipitation. S. G. C.

The Specificity of Hahn's Fluorescein Reagent for Bromine. J. H. Van der Meulen. (*Chem. Weekblad*, 1939, **36**, 702–705.)—Hahn's method for the determination of bromides (*cf. Mikrochem.*, 1935, **222**; see also Seaber, ANALYST, 1936, **61**, 14, and Grant, *id.*, p. 400), in which the bromine liberated by a mild oxidising agent, namely chloramine-T, is used to convert fluorescein into eosin, is criticised; this criticism is notably in respect of the effect of the *p*H at which the reaction takes place and of the proportion of chloramine-T used. The following modified method is suggested:—To 2 ml. of a solution containing 100 mg. of fluorescein per litre (1 ml. if only 10 to 50γ of bromide ion are involved), are added 3 ml. of a 3·1 per cent. solution of boric acid and 0·1 to 1·0 ml. of a solution of potassium bromide equivalent in concentration to 100 mg. of Br′ per litre. In this way ten standards are prepared in similar glass tubes having flat bases, the volume of each mixture being finally made up to 8 ml. Into each tube is put 1 ml. of a fresh 0·01 *N* solution of chloramine-T, prepared as required by dilution of a 0·1 *N* solution, *i.e.* containing 14 to 15 g. of a good commercial grade of chloramine-T in 1 litre of 0·01 *N* sodium hydroxide solution. After 3 minutes the excess of oxidising agent is reduced by addition of 1 ml. of a 1·25 per cent. solution of sodium thiosulphate in *N* sodium hydroxide solution. The red colour which develops is then matched against that produced from the sample in the same way. It is commonly believed that this reaction is specific for the bromide ion, but the author finds that the iodide ion also produces a red colour; this, however, is probably due to iodoeosin (erythrosin) which is produced by the action of the iodine monochloride formed as a result of the interaction of chloramine-T and the iodide. If, however, the *p*H is raised slightly by the use of a buffer solution containing 31 g. of boric acid (see above) and 8 ml. of *N* sodium hydroxide solution per litre, the bromides do not react, but in presence of an iodide a brown colour is produced immediately and changes rapidly to a red shade. In these circumstances it is advisable to buffer the solution by the addition of 1 ml. of a 0·1 *M* solution of sodium dihydrogen phosphate (presumably in addition to the boric acid and alkali), and to use 1 ml. of a solution of 20 mg. of fluorescein in 1 litre of water and 0·2 ml. of the 0·01 *N* chloramine-T solution. The reaction is satisfactory for 1·6 to 16γ of iodide ion, but if the bromide-content is small and an iodide is present, the determination of the former in the manner described above may not be wholly reliable. Exposure to sunlight, or even to bright daylight, results in an increase in the intensity of the colour produced by iodides. J. G.

Microchemical

Studies in Micro-Crystallisation in Supersaturated Solutions. A. Tschermak-Seysenegg. (*Mikrochem.*, 1939, **27**, 96–111.)—Supersaturated solutions or melts, especially those of sodium or potassium acetates, sodium thiosulphate, salol, or potassium and chromium alums, may be preserved indefinitely in absence of specific nuclei and are unaffected by the introduction of various "non-infecting" substances, especially alien crystals. The immunity persists in presence of heteromorphous crystals of other hydrates of the same substance. For the examination of the crystals under the microscope use is made of a flattened tube, 14 mm. long and 7 mm. in diameter, with a narrow extension, also flattened, 3 mm. long and 2 mm. in diameter. The tube, which is stoppered at the wide end and closed at the narrow end, is laid on its broadest side on the microscope stage. As a special method for the infecting of test solutions contained in sealed tubes deposition of crystals is promoted by freezing the solvent by local cooling. The basis of the specific action of the active nucleus is the space lattice and crystal structure. The seeding crystals and those from the solution must fit into each other, so that the seeding test for infection or non-infection may be used as a micro-method for diagnosing the coincidence, or otherwise, of the space lattice and the crystal structure. As regards energy changes on crystallisation, evolution of heat has been observed; there is also an apparent production of electrical charges in layers, even before the electrodes (a capillary electrometer is used) are reached by the zone of crystallisation. Conduction through metals yields a positive main front; through carbon a negative one. The basis of the crystallisation electricity is to be seen in the separation, from the solvent, of small particles of solution which may be regarded as liquid crystals. In the crystallisation there are combined the manifestations of morphological vector properties or the "dove-tailing" of space lattices and crystal structures which fit into one another, and of electrical vector properties or zonality. J. W. M.

Identification of Flavouring Constituents of Commercial Flavours. VIII. Semi-Micro Determination of the Amido-Nitrogen Atom in Semi-Carbazones. J. B. Wilson. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 688–690.)—The following modification of the method described by Veibel (*Bull. Soc. Chim.*, 1927, **41**, 1410; Abst., ANALYST, 1928, **53**, 53) for the determination of the amino-nitrogen atom in semicarbazones enables the determination to be made with 10 to 25 mg. of the sample. The micro-Kjeldahl digester and steam-distilling apparatus recommended are those described by Clark (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 255). The sample (10 to 25 mg. expected to contain 1 to 2 mg. of nitrogen) is heated with 5 ml. of dilute sulphuric acid (1 + 4) for 15 to 20 minutes or until the sample is completely hydrolysed. If incipient charring occurs, 1 to 2 ml. of water are added and the digestion is continued. The neck of the flask is rinsed down with 1 or 2 ml. of water, 1 ml. of 5 per cent. potassium iodate solution is added, and the mixture is boiled until iodine vapour has been completely removed. The neck of the flask is again rinsed, and the mixture is transferred to the steam-distillation apparatus with 10 ml. of water in four or five portions. The condenser outlet is immersed in 10 ml. of 0·02 *N* acid containing a little methyl red indicator. Sodium hydroxide (5 ml. of a 40 per cent. solution) is added to the mixture, and distillation is carried out for four or five minutes and, after lowering the acid liquid sealing the condenser outlet, for a further two minutes to rinse down the condenser. When distillation is complete, the acid liquid is heated to boiling-point and titrated while still hot with standard *N*/70 alkali (sodium, potassium or barium hydroxide solutions) the liquid being re-heated when the end-point is nearly reached. The titre of the acid solution is determined by the same method of titration. The alkali solution is standardised by distilling 5 ml. of a standard nitrogen solution into 10 ml. of the 0·02 *N* acid. The standard nitrogen solution is prepared by placing an amount of ammonium hydroxide equivalent to 40 mg. of nitrogen in a 100-ml. flask with a little methyl red indicator, titrating with *N*/10 acid, and diluting to 100 ml. with water. Application of the method to the determination of several pure semicarbazones showed that the semi-micro method has the same degree of accuracy as the macro-method, with a tendency towards high results. The molecular weight of the aldehyde or ketone is given by the formula $(1400{\cdot}8 \div \text{percentage of nitrogen found}) - 57{\cdot}05$ (Wilson and Keenan, *J. Assoc. Off. Agr. Chem.*, **1930**, **55**, **638**; Abst., ANALYST, **1930**, **55**, **638**).

A. O. J.

Nitrobarbituric Acid as a Reagent for the Alkaline Earth Metals. H. A. Friedland. (*Amer. Chem. Soc., Div. Microchem., Meeting*, Sept., **1939**, *Absts.*, 10.)—A saturated solution of nitrobarbituric acid in *N* hydrochloric acid is a satisfactory microscopic reagent for the detection of the alkaline earths, with each of which it forms a characteristic crystalline precipitate. It is particularly suitable for the detection of magnesium. The sensitivity of the test for various metals was:—barium, $0{\cdot}5\gamma$; calcium, $0{\cdot}5\gamma$; strontium, $0{\cdot}25\gamma$; magnesium, $0{\cdot}0007\gamma$. Precipitates with well-formed crystals were also given by ammonium, cadmium, caesium, cobaltous, cupric, lead, manganous, nickelous, potassium, rubidium, thallous and zinc ions. No precipitates were formed with aluminium, antimony, arsenious, bismuth, chromic, ferric, lithium, sodium, stannic and stannous ions.

E. B. D.

Physical Methods, Apparatus, etc.

New Light Sources for Colorimetry. F. L. Matthews, R. H. Crist and A. Knoll. (*Ind. Eng. Chem., Anal. Ed.*, **1939**, **11**, 503.)—Neon lamps provide a very intense source of illumination which is relatively cool and concentrated in a narrow spectral band.

S. G. C.

Photocolorimetric Determination of Free or Conjugated Compounds of the Sulphanilamide or Similar Type by means of Marshall's Reaction in Filtered Light. L. Servantie and G. Demange. (*J. Pharm. Chim.*, 1939, **30**, 163–170.)—In Marshall's method for the determination of sulphanilamide (*Proc. Soc. Exp. Biol. Med.*, 1937, **36**, 422) the sample is diazotised and coupled with dimethyl-α-naphthylamine, when an intense red colour is produced (sensitiveness, $1 : 10^7$). Disadvantages are the interfering colours which may be produced by biological fluids (*e.g.* blood or urine) even after defecation, and the difficulty in matching the colour, owing partly to the variable rate at which it develops in different instances, and partly to its instability. The latter objection has been overcome by buffering the solution at a *p*H of 1·7 to 1·8, and stopping diazotisation after 3 minutes by addition of ammonium sulphamate (*cf.* Marshall and Lichtfield, *Science*, 1938, **88**, 85); the former by the use of an Evelyn photo-electric colorimeter (*cf.* MacLachlan, Carey and Butler, *J. Lab. Clin. Med.*, 1938, **23**, 1273; and Evelyn, *J. Biol. Chem.*, **1936**, **115**, **63**). This is possible because the red colour has an absorption range of $550{\cdot}0$ to $500{\cdot}0m\mu$ (maximum, $526{\cdot}0m\mu$), whilst the absorption of the interfering colours is in the region of 400 and $600m\mu$, and can be eliminated by means of filters. The red colour then satisfies the Beer–Lambert law, and the concentration of the sulphanilamide may therefore be calculated from measurements of the optical densities in the usual way, a standardisation-curve relating these two variables being first constructed from solutions of known concentrations.

The method is rapid and its sensitiveness is 1 per cent. with blood, human milk and urine. The following is the procedure for blood containing 1 to 20 mg. per litre of sulphanilamide:—To 0·50 g. of sulphamic acid in a 100-ml. flask are added 10 ml. of water and sufficient ammonia (about 0·8 ml.) to neutralise the acid to methyl red (used as an outside indicator); 13·80 g. of sodium dihydrogen phosphate are then added, and the volume is made up to 100 ml. This is a buffered solution of ammonium sulphamate. The Marshall reagent is a mixture of 1 ml. of dimethyl-α-naphthylamine and 250 ml. of 95 per cent. alcohol, and it should be protected from heat and light. The blood is treated with potassium oxalate in the usual way, and 2 ml. of the resulting solution are introduced slowly, with agitation, into a centrifuge-tube containing 6 ml. of a 0·05 per cent. solution of saponin (to ensure haemolysis). To the mixture are added 2 ml. of 20 per cent. trichloroacetic acid, and after 10 minutes the mixture is centrifuged or filtered, and 3 ml. of the clear liquid are collected. *Direct method.*—To 2 ml. of this are added 3 ml. of water and 0·5 ml. of a 0·10 per cent. solution of sodium nitrite followed, after 3 minutes, by 1 ml. of the buffered solution of ammonium sulphamate, and after a further 2 minutes, by 3 ml. of the Marshall reagent and 1 ml. of water. A blank test should be made with a mixture of 1 ml. of the trichloroacetic acid and 4 ml. of water. *Determination after hydrolysis.*—To 1 ml. of the liquid which remains after defecation and filtration (see above) is added 1 ml. of *N* hydrochloric acid, and after 45 minutes on the water-bath (under conditions which minimise evaporation) the mixture is cooled, and 2 ml. of water are added, followed by the nitrite and other reagents as described above, except that 2 ml. of the buffered sulphamate solution are used. Values obtained from a patient receiving 1·20 g. of carboxysulphamido-chrysoidine per day were, after administration of 3·20 and 5·20 g., respectively:—In the urine, 0·053 and 0·145; blood, 0·0043 and 0·0041; milk, 0·0033 and 0·0037; urine of nursling, 0·016, — g. of sulphanilamide per 1000 g. (obtained by the direct method). J. G.

Spectroscopical Examination of the Mineral Constituents of Honey, Part I. G. Gorbach and F. Windhaber. (*Z. Unters. Lebensm.*, 1939, **77**. 337–346.)—In a study of the emission spectrum of honey it was not found necessary or even advisable to remove the organic matter by ignition. A drop of honey was placed in a depression in the lower pole of the carbon arc of a Zeiss spectrograph arranged to photograph the spectrum in the region 210 to 460$m\mu$. The spectrum of the carbon arc was first photographed and underneath it the spectrum of the arc after the addition of honey, and finally a wave-length scale (calibrated by means of the cadmium spectrum) was photographed above and below the double spectrum. The number of lines and the number of intense lines given by each element present were recorded for each sample of honey. The method was applied to a number of samples of native and foreign honey with good results, the line spectrum being as characteristic for each sample as the pollen analysis. The method is useful for statutory purposes, *e.g.* to establish the identity or non-identity of two samples. Wild honeys show numerous lines, floral honeys fewer lines, and by mere inspection of the line spectrum it can be decided whether a sample is pure wild honey, pure flower-honey or a mixture of both. A number of imported flower-honeys contained, besides sodium and potassium, the cations calcium, magnesium, iron, manganese, copper, nickel and the phosphate and silicate anions, all of which, with the exception of nickel, have been detected and determined by other workers. The number of elements present varied from 11 to 14, the following additional elements (in order of frequency) being present in some samples:—barium, cobalt, zinc, palladium, vanadium, arsenic, strontium, aluminium and tungsten. Two samples of honey dew (tamarisk and oak) gave 25 and 26 elements respectively, the elements being the same as for the wild honeys. An artificial product (glucose syrup) gave 12 elements, *viz.* calcium, magnesium, iron, manganese, phosphorus, silicon, copper, nickel, barium, tungsten, silver and strontium; it thus resembled the floral honeys, but was distinguished from them by quantitative differences. The addition of wild honey to floral honey causes an increase in the number of elements detectable in the spectrum. No relation between the mineral constituents and the colour of the honey was deducible (*cf.* Schuette and Remy, *J. Amer. Chem. Soc.*, 1932, **54**, 2909; Abst., ANALYST, 1932, **57**, 578). A. O. J.

Reviews

VOLUMETRIC ANALYSIS. By A. J. BERRY. Fifth Edition. Pp. 196. Cambridge University Press. 1939. Price 7s. 6d.

This new and revised edition, which has appeared after a ten years' interval, has been amplified by the inclusion of a chapter on gas analysis and a good deal of matter relating to modern developments. The object, as with the previous editions, was to provide a practical book, primarily for the author's students at Cambridge, which would be useful up to a moderately advanced stage of work, after which reference to specialised or larger textbooks would become necessary. The standard processes—titrations with permanganate, dichromate, iodine, silver nitrate and so on are first dealt with (65 pp.); there are chapters on acid-alkali titrations, theory of indicators and various volumetric determinations (45 pp.), and applications and examples of volumetric processes are given (17 pp.). There is a chapter on simple gravimetric methods (17 pp.), and also a new one on gas analysis (11 pp.).

Throughout the book the chemical basis of the processes is explained carefully, and generally sufficient details are given to enable students to carry out determinations in an intelligent manner. Directions of the cookery book variety are conspicuously rare. The commendable style in this respect disarms a criticism which might be made that in some places practical details are a little vague; in connection with the iodimetric method for copper, for instance, it is stated that a "few crystals" of potassium iodide are to be added, whereas an excess over that required to precipitate the copper as cuprous iodide is necessary. Among useful features are the quantitative determination of sodium by precipitation as dihydroxytartrate, which can be dissolved and subsequently titrated with permanganate, and the titration of permonosulphuric and perdisulphuric acids in mixtures.

Modern developments are contained in a special chapter (35 pp.) which deals principally with the newer *p*H indicators, oxidation-reduction and adsorption indicators, standard ceric sulphate solution, methods involving iodate and bromate and the use of liquid amalgams for reduction. Electrometric methods are not given. The segregation of modern developments is probably advantageous for students following a definite course. One notices, however, a few instances of lack of co-ordination with the traditional methods described in the earlier part of the book. Thus the increased usefulness of potassium dichromate brought about by the introduction of internal indicators, such as diphenylamine sulphonic acid, is dealt with in this chapter, but it was stated earlier that dichromate possesses the disadvantage of requiring an external indicator, such as ferricyanide. Granulated zinc is used for reducing ferric salts (p. 20), but later on (p. 102) liquid amalgams are stated to have rendered granulated zinc obsolete for reduction purposes. It should be understood that the points on which such criticisms are possible are of very minor importance and do not seriously detract from the undoubted value of the book as a whole, which, at its modest price, is one that can be strongly recommended.

S. G. CLARKE

THE WAR GASES, CHEMISTRY AND ANALYSIS. By Dr. MARIO SARTORI, translated from the Second Enlarged Italian Edition by L. W. MARRISON, B.Sc., A.I.C. Pp. 360 + xii. London: J. & A. Churchill, Ltd. 1939. Price 21s.

Dr. Sartori is Chemist of the Italian Chemical Warfare Service, and it is evident that he has made a thorough study of these military atmospheric poisons and especially of the chemical literature dealing with them. He seems to have studied every scattered reference of any importance in German, French, English, Russian and Italian, and he has gathered the information together in a convenient form. The first Italian edition appeared in 1933, and a German translation by Dr. Hans Klumb was published in 1935. This second edition contains a considerable amount of additional information, and the number of substances dealt with is increased from 49 to 64, but the added 15 "gases" do not appear to be of much practical importance. There are about a thousand references to original papers, and these will be of great assistance to those who require fuller information. Although there have been a number of books published on chemical warfare during the last twenty years, they deal mostly with its military or medical aspects; this is the only work which gives full information, so far as it is available, about preparation, manufacture and chemical analysis.

The first chapter is on the principal properties of the war gases, starting with the physio-pathological: the lower limit of irritation, the limit of insupportability and the "mortality product." The last has been measured by experiments on animals, in Germany on cats, and in America on dogs and mice. As might be expected, the results do not run parallel, and those for human beings would probably be different again.

The physical properties discussed are vapour tension, volatility, boiling-point, melting-point and persistence. All these, except the melting-point, depend on the vapour tension or the vapour tension combined with the molecular weight. Unfortunately, it appears that the value given for the vapour tension of a substance at a given temperature is often quite different from that which has been used for calculating the volatility of the same substance at the same temperature.

The stability of war gases is also discussed in Chapter I. Chapter II deals with the relation between chemical structure and aggressive action, but it cannot be said that definite rules have been discovered whereby the action can be predicted. The discussion is, however, interesting. Chapter III describes various methods of classifying these substances according to their physical properties, tactical use, pathological action or chemical composition. The choice of the system adopted will naturally depend on the purpose for which the classification is made. In this book the war gases are arranged according to their chemical relationships and similarity of structure.

The second part of the book comprises about nine-tenths of its contents, and consists of twelve chapters each devoted to a separate class of compound. For each compound information is given, if available, about its discovery, preparation, manufacture, physical and chemical properties and physiological action. At the end of each chapter methods of analysis are usually given.

The translation has been well done and there are few misprints, but there is an obvious slip in the formula on the last line of p. 338, and the molecular weight on the last line of p. 340 should be 268, not 272. This book will be indispensable to all chemists who have to deal with war gases. ARTHUR MARSHALL

USES AND APPLICATIONS OF CHEMICALS AND RELATED MATERIALS. Compiled and Edited by THOMAS C. GREGORY. Pp. vi + 665. New York: Reinhold Publishing Corporation; London: Chapman & Hall. Price 60s. net.

There are many books of reference to which one may turn to find the materials used for a particular purpose. On occasion the converse is required and, while there is generally no difficulty in finding the chief uses of any commercial substance, many minor applications are known only to the initiated and references are scattered. The present volume is an attempt to collect and collate such information and, as the sub-title indicates, it is "a guide to the current industrial uses, potential application and sales possibilities of 5167 products."

The material is founded on data published in the *Oil, Paint and Drug Reporter* between 1922 and 1939, and is largely composed of references to inorganic chemicals, organic chemicals, drugs and pharmaceutical products, with related substances such as metals, petroleum products, minerals, animal and vegetable oils, essential oils, and so forth. Each article described has the common synonyms and foreign equivalents noted. Then follow the uses under a number of sub-headings dealing with branches of industry or science. No fault can be found with such a convenient arrangement, but in certain instances it has led to duplication which editing should have corrected. One liquid is described as a solvent under 35 separate headings, and it is not, therefore, surprising that under "Miscellaneous" it is described as a "general solvent."

Some of the information is almost useless or is misleading. Thus the only detail for quite a number of substances is "claimed as a new pharmaceutical" or "suggested for use as antiseptic," and several inert substances used as fillers are quoted as ingredients of antiseptics, insecticides, fertilisers, or other products. There is not much point in stating that cinchonine is the starting point in making cinchonine acetate, . . . cinchonine valerianate, 26 salts being mentioned, or that copper is used as copper-smithing material in fabricating (*a*) over 150 named plant units—from agitators to yeast equipment, and (*b*) apparatus for over 30 types of plant using these units—from bakeries to wood distillation plant. The sole use given of activated alumina is for dehydrating processes and of ascorbic acid as a photographic developer.

Some surprising uses have been noted, *e.g.*:

Acetylene—reagent in making inks.
Benzoic acid—reagent in making iodised pharmaceutical derivatives.
Carbon dioxide—a drying agent in making various chemicals, a reagent for digesting oxidisable substances, a reagent in packing tobacco in tins.
Hydrofluoric acid—reagent for making yeast.
Potash alum—ingredient of margarines.
Quartz—ingredient of ammonium persulphate compositions for the treatment of flour.
Radium bromide—used in making fertilisers and for other agricultural purposes.
Red oxide of iron—reagent in making mineral waters.
Stearin—ingredient of oil-soluble dyestuffs.
Talc—bleaching agent for treating barley.

Clearly there has been little attempt to edit, from a technical point of view, vague statements and loosely worded claims appearing in patent specifications and advertising matter.

It is difficult to estimate the completeness or otherwise of the references. Nearly all the articles specially looked for were found to be mentioned, but it was observed that there is no specific reference to copper oxychloride, cyclohexanol, ferrous sulphate, metaphenylenediamine, paraphenylenediamine (the picrate and the salt of meta-4-xylenol are mentioned), rotenone, and sodium hexametaphosphate.

The book contains a mass of information unavailable elsewhere in a collected form and must be of practical value to many business people. It is hoped to publish supplementary volumes at suitable intervals. J. R. NICHOLLS

MICRO-ORGANISMS AND FERMENTATION. By the late ALFRED JØRGENSEN. Sixth Edition. Revised and largely re-written by ALBERT HANSEN and AAGE LUND, with the asistance of C. AINSWORTH MITCHELL. Pp. xi + 416. Chas. Griffin & Co., Ltd. 1939. Price 30s.

Alfred Jørgensen's book has long been regarded as one of the classics in the literature of micro-biology. It was originally written to serve as a textbook for the courses in fermentation and technical bacteriology held in the Jørgensen Laboratory of Fermentation and embraces the general science of bacteriology and its special application to the fermentation industries and dairying. While the book has been very largely re-written, its general plan is essentially unchanged. Instead of the original illustrations, which were mostly from old drawings by Hansen, a series of excellent photomicrographs (40 plates with 137 illustrations) has been appended, demonstrating bench technique and various yeasts, moulds and bacteria.

The book opens with a short preface followed by a historical introduction. Chapter II deals with general features of morphology and physiology—cell structure, reproduction, enzymes and co-enzymes, assimilation, dissimilation, splitting and oxidative fermentations. Chapter III deals with laboratory equipment. Here we find a very excellent description of the structure of the modern compound microscope and auxiliary apparatus, such as counting chambers, micrometers and drawing apparatus. Chapter IV describes the preparation of nutrient media. Chapter V deals with sterilisation and disinfection, and includes sterilisation by filtration, the modern Seitz asbestos filters, and disinfection with ammonium fluoride and chloramine-T. Chapter VI gives an account of laboratory technique and includes methods of staining and counting, the preparation of pure cultures, anaerobic cultivation and the preservation of cultures. Chapter VII (43 pages) is devoted to the moulds. In addition to a general account of their characteristics, methods of reproduction, products of dissimilation, classification, identification, and so forth, a good account is given of their industrial applications, as in the saccharification of rice starch, in the cheese industry, in the manufacture of citric acid and in the use of *Botrytis cinerea* in the wine industry. Chapter VIII (104 pages) is concerned with the yeasts. The various sections deal with the morphology, anatomy and reproduction of the yeast cell; the physiology of yeasts; their enzymes; nutrient requirements; various types of fermentations; influence of external factors; variations of yeasts; occurrence in nature; methods of study; taxonomy of yeasts and yeast-like fungi; culture yeasts; brewery yeasts, including infections in brewing plant and their detection; distillery and pressed yeasts; wine-yeasts; wild yeasts; other species of *Saccharomyces*; other genera of yeasts occurring in the fermentation industries and yeast-like fungi. This is a most interesting chapter and the outcome of nearly 50 years of study and teaching in the Jørgensen Laboratory of Fermentation with a survey of contemporary work. That section describing variations of yeasts effected by external conditions and the use of pure yeast cultures in the brewery is of special interest, for Jørgensen made important contributions to the foundation and development of modern brewing and was the first to introduce the use of pure cultures in top-yeast fermentation. Chapter IX (105 pages) deals with bacteria, first in general, discussing their occurrence, morphology, reproduction, biology and physiology, then, more particularly, classification and nomenclature, with special reference to those bacteria of technical importance:—the acetic acid bacteria; the lactic acid bacteria occurring in the dairy and brewing industries, in distilleries, in wine and sugar manufacture; the propionic acid bacteria; the *coli-aerogenes* group; alkali-producing bacteria and thermobacteria (which, as is pointed out, are to be distinguished from "termo" bacteria); spore-bearing bacteria, aerobic and anaerobic. A good account is given of the injurious lactic acid bacteria occurring in the brewery, including the sarcina and pediococci described by Claussen. Chapter X deals with micro-organisms in water and air. There follow an appendix in which nutrient media, stains and reagents are described, a bibliography, author index and subject index.

The book is admirably arranged and very well written, Dr. Ainsworth Mitchell has given his able assistance in rendering the language more idiomatic and has added some notes, the type and paper are excellent, and the book has an attractive binding. It will be found of value to many workers in the various fields of microbiology and of the greatest use to students and workers in the fermentation industries.

D. R. WOOD

DER VERKEHRSUNFALL. By Professor GERHARD BUHTZ. Pp. vii + 231, with 58 Diagrams and Illustrations. Stuttgart: Ferdinand Enke. 1938. Price 14RM., bound 15.60RM.

This work is a comprehensive treatise embodying the results of fifteen years' experience in the investigation of the causes of motor-traffic accidents, with special reference to alcoholic intoxication. This is a causative factor more frequently than official statistics suggest, because these statistics tend to include only those instances in which intoxication has been obvious to the police official. The author discusses fully the physiological effects of the consumption of relatively small amounts of alcohol, insufficient to produce intoxication in the popular sense of the word but sufficient to affect those faculties of accurate judgment, instant response to external stimuli and sustained mental concentration which are the foundations of skilled driving. Much experimental work by different investigators is quoted to substantiate the conclusions arrived at concerning the precise effects of alcohol upon the physical, mental and psychological reactions of the driver to traffic emergencies.

The determination of alcohol in the blood by Widmark's microchemical method is described in ample detail, and the conclusions to be drawn from the results of such determinations are fully and logically discussed, especially in their relation to clinical symptoms and other evidence of intoxication. Pathological states which may simulate intoxication are also discussed, as is also the question whether the use of other stimulants or medicaments (for example, coffee, tobacco, aspirin, insulin) influences the degree of intoxication or vitiates the results of blood-alcohol determinations. Since the author is anxious that his work shall be a contribution towards the solution of traffic problems, he studies its relation to the existing legislation controlling motor traffic. So forcibly is he impelled towards the opinion that the motorist's only safe course is total abstinence for a period before the journey and during it, that he finds it necessary to assure his readers that his insistence on this is not to be mistaken for anti-alcohol propaganda.

A large section of the work deals with such evidence as may be afforded by clues at the place of the mishap, on the vehicle or on the clothing of the persons involved, and by the examination of wounds and by investigations *post mortem*. Such considerations are presented with commendable caution and are exemplified by a number of actual cases briefly but clearly described; a few of these serve as warnings against hasty deduction before the whole of the available evidence is assembled.

The forensic chemist, the biochemist, the medical man, the lawyer, the legislator, the police authorities and the layman who is concerned in any way with traffic problems will find much of absorbing interest in this book. There is a terminal bibliography of 384 references. The book is clearly printed, and the language presents no difficulty to those accustomed to the reading of German technical literature.

A. O. JONES

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